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EXPERIMENTAL CURRICULA IN CHEMISTRY, A REPORT OF THE A.C.C.C.  
CONFERENCE ON CURRICULUM EXPERIMENTATION (CHICAGO, OCTOBER  
1963).

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ADVISORY COUNCIL ON COLL. CHEMISTRY

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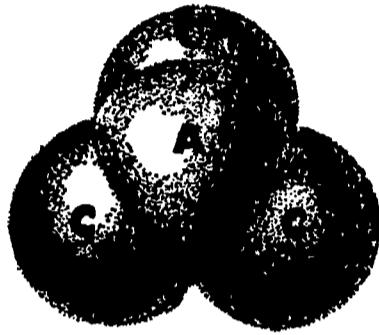
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INNOVATION, INNOVATION, CURRICULUM DEVELOPMENT, PROGRAM  
DEVELOPMENT,

FOUR PROGRAMS ARE IDENTIFIED AND DESCRIBED AS  
REPRESENTATIVE OF THE EXPERIMENTATION BEING CONDUCTED IN THE  
UNDERGRADUATE CHEMISTRY CURRICULUM IN AMERICAN HIGHER  
EDUCATION. (1) THE UNIVERSITY OF ILLINOIS AND THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY REQUIRE THAT A STUDENT  
TAKE A GROUP OF "CORE" COURSES WHICH PROVIDE, RELATIVELY  
EARLY IN HIS CHEMISTRY STUDIES, A GENERAL BACKGROUND FOR MORE  
SPECIALIZED WORK. (2) BROWN UNIVERSITY'S PROGRAM IS ORGANIZED  
SO THAT THE STUDENT HAS A BACKGROUND IN DESCRIPTIVE AND  
PHYSICAL CHEMISTRY, CALCULUS, AND DIFFERENTIAL EQUATIONS BY  
THE END OF HIS SECOND YEAR AND UNDERTAKES QUANTITATIVE  
ANALYSIS OR ORGANIC CHEMISTRY IN HIS THIRD YEAR. (3) THE  
CHEMISTRY SEQUENCE AT BELOIT COLLEGE BEGINS WITH AN  
INTERDISCIPLINARY COURSE IN PHYSICS AND PHYSICAL CHEMISTRY.  
(4) EARLHAM COLLEGE ORGANIZES ITS COURSES AROUND CENTRAL  
CONCEPTS RATHER THAN THE TRADITIONAL SUBJECT MATTER  
DIVISIONS. IN ADDITION, HARVARD IS EXPERIMENTING WITH AN  
ACCELERATED PROGRAM TO PREPARE TALENTED STUDENTS FOR SENIOR  
AND GRADUATE WORK BY THE BEGINNING OF THEIR JUNIOR YEAR.  
(ADVANTAGES OF EACH PROGRAM ARE DISCUSSED.) (AD)

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# *Experimental Curricula in Chemistry*



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INFORMATION

*A report prepared by the*

COMMITTEE ON CURRICULUM AND  
ADVANCED COURSES

*of the*

ADVISORY COUNCIL ON COLLEGE CHEMISTRY

JC 670 581

# *Experimental Curricula in Chemistry*

*A Report of the A.C.C.C. Conference*

## **CURRICULUM EXPERIMENTATION**

**CHICAGO, ILLINOIS**  
**OCTOBER, 1963**

This report, compiled by David N. Hume, Professor of Chemistry, Massachusetts Institute of Technology, is one of a series designed to aid in improving the teaching of college chemistry. This report, and other activities of the Advisory Council on College Chemistry, are supported by a grant from the National Science Foundation.

All persons on the Council "Newsletter" mailing list are being sent copies of this report. A limited number of additional copies are available free of charge from:

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## I INTRODUCTION

Widespread dissatisfaction exists with the traditional chemistry curriculum for chemistry majors which is used at many American colleges and universities. A survey of the 125 departments listed in the American Chemical Society's "Directory of Graduate Research," carried out in the spring of 1963 by a committee of the Advisory Council on College Chemistry, revealed that 106 of the 119 institutions replying had made, or were planning to make, changes which they described as "major" in their curricula for chemistry majors.

It is evident that the pattern which has served so well for many years is no longer felt to be satisfactory for the teaching of present-day chemistry. The question of what to substitute for the conventional approach is one which is not easily answered. Departments all over the country have been experimenting with everything from relatively simple rearrangement of existing courses to complete restructuring of the subject matter organization, with drastic changes in teaching philosophy. These developments are inevitably influenced by local needs and constraints, and have varying degrees of effectiveness. There is one characteristic in common, however. They all involve a large amount of work on the part of the faculty members concerned.

The expenditure of time involved in development of a really new curriculum is a factor which gives pause to many who would like to see different approaches tried. Not every department can afford to commit staff facilities to experiments with untried teaching methods which may or may not represent clear-cut improvements. A change in one course leads to the necessity for changes in others, lest the whole structure of the curriculum be put out of balance. A complete modernization involves both thinking through anew the aims and objectives of the curriculum and evaluation of many alternatives in the light of contemporary needs, local and national. Those who have undertaken such programs have not found it easy, and there is a felt need for means of communicating the ideas and experiences which have developed.

In considering ways in which the Council might be most effective in carrying out its objective of the improvement and strengthening of chemistry at the college level, the implementation of curriculum experimentation seemed to be primary. The Panel (later called Committee) on Curriculum and Advanced Courses was, therefore, charged with the responsibility of organizing a conference in which a group of representatives from leading institutions might get together with several individuals who had been instrumental in developing new curriculum approaches. Preliminary work by the Panel identified what seem to be four well defined approaches which represent major changes in direction and which have been in actual operation for some time. The conference was, therefore, planned around a rather detailed exposition of philosophy, objectives, methods, and results of these four plans with the aim of getting needs into clear focus and appraising the advantages and disadvantages of the various proposed solutions.

Fourteen universities and three colleges were represented when the Conference convened in Chicago on October 17, 1963. The participants, representing a wide range of geographical distribution and type of institution, were the following:

Benfey, O. Theodor, Earlham College  
Clapp, Leallyn B., Brown University  
Davidson, Norman, California Institute of Technology  
DeFord, Donald D., Northwestern University  
Fenton, Stuart W., University of Minnesota  
Fuller, Edward C., Beloit College  
Hammett, Louis P., Columbia University  
Hill, Richard K., Princeton University  
Hornig, James F., Dartmouth College  
Hume, David N., Massachusetts Institute of Technology (Chairman)  
Laitinen, Herbert A., University of Illinois  
Larsen, Edwin M., University of Wisconsin  
Margrave, John L., Rice University  
McMillan, William G., Jr., University of California at Los Angeles

Nachtrieb, Norman, University of Chicago

Nash, Leonard K., Harvard University

Tamres, Milton, University of Michigan

Wilder, Pelham, Jr., Duke University

Yankwich, Peter, University of Illinois

Mays, John M., National Science Foundation (observer)

The four characteristic developments presented and discussed in detail were—

- (1) The Illinois-Massachusetts Institute of Technology Plan, presented by H. A. Laitinen
- (2) The Brown Plan, presented by L. B. Clapp
- (3) The Combined Physics and Chemistry Course, presented by E. C. Fuller
- (4) The Earlham Plan, presented by O. T. Benfey

L. K. Nash described informally an experiment being carried out with a small group of students at Harvard University.

Consideration of the details of these very varied curriculum approaches and the special considerations which prompted them brought into much clearer focus many of the problems involved in developing the optimal curriculum. Among the conclusions reached by the group was the recommendation that the details of the curriculum experiments discussed in the conference be made widely available to chemists interested in the improvement of their teaching, and that the discussion and conclusions be given similar widespread availability. The present report is the result of that recommendation.

The descriptions of the several curricula and the background material pertaining to them have been written by Drs. Laitinen, Clapp, Fuller, and Benfey, who presented them at the Conference. The introduction, summary and general editing was done by D. N. Hume. The Committee offers this report in the hope that it may make easier the work of those who are undertaking the arduous task of curriculum revision.

**The Committee on Curricula and Advanced Courses  
ADVISORY COUNCIL ON COLLEGE CHEMISTRY**

D. N. Hume (Chairman)  
L. B. Clapp  
L. P. Hammett  
E. M. Larsen  
M. Tamres

## II. THE ILLINOIS-MASSACHUSETTS INSTITUTE OF TECHNOLOGY PLAN

H. A. LAITINEN, *University of Illinois*, Urbana, Illinois

The curriculum described here is characteristic of the approach now used by a number of institutions, particularly the larger universities. One of the first to develop such a plan was MIT, which revised its chemistry offerings along these lines in 1957, and has continued in this method of operation ever since. The specifics of the curriculum vary from institution to institution, but the essential features tend to be the same. The program at the University of Illinois is given as representative, and its history, philosophy, and mode of operation are, therefore, presented in some detail.

### THE UNIVERSITY OF ILLINOIS CHEMISTRY CURRICULUM

Until 1960, the chemistry curriculum at the University of Illinois followed a traditional pattern, with required courses arranged essentially in the order of historical development of the various branches of chemistry.

Two sequences of general chemistry (including qualitative analysis) were offered, to allow for differences in the level of preparation of the entering student, requiring respectively two or three semesters. A five-hour course of traditional quantitative analysis, two semesters each of organic and physical chemistry, and a three-hour course in instrumental analysis in the senior year completed the basic requirement. Senior research and advanced electives were available in the various branches of chemistry (including biochemistry). Inorganic chemistry was not strictly required although most students elected a three-hour lecture course in the senior year. Courses in chemical literature, history of chemistry, and economics were specific requirements.

Several disadvantages of this curriculum had become increasingly apparent. With improvements in high school chemistry, mathematics, and physics it appeared possible to accelerate progress into physical chemistry and to upgrade the general chemistry course so as to present a greater challenge to the well-prepared students. Above all, pressures were felt for increasing the flexibility of the curriculum, and allowing at an earlier level divergence towards ultimate specialization in fields as diverse as chemical physics and chemical biology. In planning the new curriculum, therefore, it was decided to set as requirements a minimum "core" of courses that could be generally agreed upon as needed by *all* types of chemists (and by chemical engineers). These requirements would be essentially completed by the middle of the third year by well-prepared students, and by the end of the third year by students of average preparation.

The following features of the revision deserve mention:

1. The three-semester sequence of general chemistry was dropped, and both semesters of the two-semester sequence (Chemistry 107-108) are now offered each term. Chemistry majors entering without high school chemistry (an unusual situation) are required to take a semester of lower-level general chemistry (Chemistry 101) before entering Chemistry 107-108. Thus the flexibility of the general chemistry course was increased, and attention could properly be focused on a single professional sequence for chemistry and chemical engineering students. More efficient utilization of special laboratory equipment was also realized.

Introduction of exact quantitative techniques into general chemistry was deemed essential to compensate for loss of laboratory time in quantitative analysis. At first, the quantitative experiments were taught as a five-week portion of the second semester laboratory, devoted to experiments stressing quantitative analytical techniques, particularly gravimetric and volumetric operations. At present, efforts are under way to spread the quantitative work more uniformly throughout the year. Emphasis is placed upon technique and accuracy, but the objectives of the experiments are those of a general chemistry course (e.g., determinations of equivalent weight and evaluation of the Faraday) rather than analysis of unknowns. Emphasis on qualitative analysis, especially on systematic schemes, has been diminished.

2. The organic chemistry course now comes during the second year, and the laboratory course has been upgraded with respect to techniques, in particular with the introduction of standard taper glassware and semi-micro experiments with increased emphasis on quantitative techniques.

3. The physical chemistry lecture course had undergone a thorough revision in the recent past, resulting in increased emphasis on quantum mechanics, statistical thermodynamics and molecular structure, and decreased emphasis on topics such as ionic equilibria and electrochemistry that are now covered in the analytical courses. In the new curriculum, physical chemistry is started in the second half of the sophomore year (together with the second semester of organic chemistry) and continued in the junior year.

The laboratory work generally lags a semester behind the lectures. Thus the second semester laboratory normally follows a semester of analytical chemistry.

4. The analytical chemistry courses have been drastically revised. The previous 5-hour quantitative analysis course in the sophomore year and the 3-hour instrumental analysis course have been combined to give a new 5-hour course in analytical chemistry (Chemistry 321) in the junior year. The lecture material includes some topics which had formerly been taught in physical chemistry (conductance and transference, electrode potentials, ionic equilibria) as well as topics previously covered in quantitative analysis and instrumental analysis. As can be seen in the outline below, the general approach is at an advanced level, making full use of the background gained in prior courses in organic and physical chemistry.

In our experience, the sophomore quantitative analysis course suffered from the following handicaps: (a) the students lacked organic chemistry so that only inorganic analysis could be taught; (b) a great deal of lecture and discussion time was spent on repetition of material (e.g., equilibrium, pH, and stoichiometry) which had already been covered to some extent in general chemistry; (c) a great deal of laboratory time was spent in acquisition of laboratory skills rather than in using modern analytical techniques, both chemical and instrumental; and (d) the students lacked sufficient background in physics, mathematics, and physical chemistry to permit a proper discussion of instrumental methods. The senior level instrumental analysis course suffered from a lack of time to do more than introduce a variety of instrumental techniques and to illustrate the fundamentals of the various measurements by suitable experiments. With only one afternoon of laboratory per week, the students never had occasion to choose among the various techniques for the solution of actual problems. Coming so late in the curriculum, the instrumental analysis course could not serve as a background for senior research.

The new course was designed to take advantage of the students' previous quantitative laboratory experience, as well as their background in organic and physical chemistry. With nine hours of laboratory per week (two long afternoons) it is planned that about half of the total time should be used in experimentation on fundamentals of chemical measurements (using both instrumental and chemical methods), and the other half should be devoted to the solving of individual problems. The problems are of two types, those originating with a sample and those originating with a stated objective. The first type is illustrated by a sample of a Bureau of Standards alloy to be analyzed for a minor constituent by a method to be chosen by the student with approval by the instructor. The second type is illustrated by a study of the effect of a reaction variable on the stoichiometry of a reaction, or the completeness of a separation. By spacing several groups of laboratory periods for individual problems throughout the semester, the laboratory work can be coordinated with the lectures. With the aid of a Course Content Improvement project (supported by NSF) the new experiments and individual problems required for laboratory instruction are currently undergoing further development. A separate course in instrumentation is available as an elective for seniors. A second semester, 3-hour course stressing quantitative organic functional group analysis, both chemical and instrumental, and multistage separation methods such as gas chromatography, is also offered as an elective.

5. A three-hour lecture course in inorganic chemistry, previously a senior elective, is now a required course in the junior year.

6. Specific requirements in chemical literature, history of chemistry and economics have been replaced by all-University requirements of six hours each of electives in social sciences and humanities. It is intended that the students gain familiarity with the chemical literature through reading assignments in the various courses rather than through a special course.

The new curriculum in chemistry is summarized below. All the chemistry courses listed are also required in the two chemical engineering curricula (engineering option or physical sciences option).

**UNIVERSITY OF ILLINOIS COURSE REQUIREMENTS  
FOR THE DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY**

A total of 130 hours of credit, not counting the first two years of physical education, as outlined below, is required for graduation.

**FIRST YEAR**

<b>FIRST SEMESTER</b>	<b>TOTAL: 16 HOURS</b>
Chemistry 107—General Chemistry <sup>1</sup>	5
Language—usually German <sup>2</sup>	4
Mathematics 122—Analytical Geometry	4
Rhetoric 101—Rhetoric and Composition	3
Physical Education	(1)

<b>SECOND SEMESTER</b>	<b>TOTAL: 17 HOURS</b>
Chemistry 108—General Chemistry and Qualitative Analysis	5
Mathematics 132—Calculus	5
Physics 106—General Physics (Mechanics)	4
Rhetoric 102—Rhetoric and Composition	3
Physical Education	(1)

**SECOND YEAR**

<b>FIRST SEMESTER</b>	<b>TOTAL: 16 HOURS</b>
Chemistry 234—Organic Chemistry	5
Language	4
Mathematics 142—Calculus	3
Physics 107—General Physics (Heat, Electricity, and Magnetism)	4
Physical Education	(1)

<b>SECOND SEMESTER</b>	<b>TOTAL: 16 HOURS</b>
Chemistry 336—Organic Chemistry	3
Chemistry 342—Physical Chemistry	3
Physics 108—General Physics (Sound, Light, and Modern Physics)	4
Physical Education	(1)
Electives <sup>3</sup>	6

**THIRD YEAR**

<b>FIRST SEMESTER</b>	<b>TOTAL: 17 HOURS</b>
Chemistry 315—Inorganic Chemistry	3
Chemistry 321—Analytical Chemistry	5
Chemistry 343—Physical Chemistry Laboratory	1
Chemistry 344—Physical Chemistry	3
Electives <sup>3</sup>	5

<b>SECOND SEMESTER</b>	<b>TOTAL: 16 HOURS</b>
Chemistry 345—Physical Chemistry Laboratory	1
Electives <sup>3</sup>	15

<sup>1</sup> For students without entrance credit in chemistry, the required sequence of courses is Chemistry 101, 107, 108. For students with entrance credit in chemistry, but without adequate preparation for Chemistry 107, the required sequences of courses is Chemistry 102, 107, 108.

<sup>2</sup> The minimum language requirement in the chemistry curriculum is the equivalent of two years of college work in German, or of one year of college work in German and one year in Russian. When a student does not offer work in either of these two languages for entrance, the required second year of language is to be taken in the fourth and fifth semesters in place of the equivalent number of elective hours.

<sup>3</sup> Specific requirements, with regard to the electives, are as follows: (a) eight hours from 300-level courses in chemistry in addition to those specifically required above, with at least two semester hours of the eight laboratory work; (b) twelve additional hours of electives chosen from advanced courses in chemistry, physics, mathematics, and/or biological sciences; (c) six semester hours each in humanities and social sciences.

## FOURTH YEAR

FIRST SEMESTER  
Electives<sup>3</sup>

TOTAL: 16 HOURS  
16

SECOND SEMESTER  
Electives<sup>3</sup>

TOTAL: 16 HOURS  
16

## COURSE CONTENT OUTLINES

### CHEMISTRY 107, GENERAL CHEMISTRY (First Semester)

Sessions: 2 lectures, 3 recitations, 4 hours laboratory per week.

Prerequisite: Analytical geometry, credit or concurrent enrollment; good high school chemistry.

Typical Texts and Manuals: Andrews and Kokes,<sup>4</sup> Brown,<sup>5</sup> Drago and Brown,<sup>6</sup> Waser.<sup>7</sup>

<i>Lecture</i>	<i>Topic</i>
1-2	Matter, energy, physical and chemical changes, nature of electron, atomic nucleus, elements and compounds.
3-4	Atomic weights, weight relationships in chemistry.
5-6	Kinetic theory of gases, gas law problems.
7	Heat capacities of gases, distribution of molecular velocities, nonideal behavior.
8	Introduction to thermodynamics.
9	Quantum theory: black body radiation, photoelectric effect, Bohr atom, atomic spectra.
10	DeBroglie equation, ionization potentials, quantum numbers, electron spin.
11	Electronic structure of elements, radii of atoms and ions.
12	Ionic bond, lattice energies.
13	Electrolytic solutions, Faraday's laws.
14-15	Covalent bond. Hydrogen molecules, hybridization of atomic orbitals.
16	Lewis structures. Resonance, partial ionic character, electronegativities.
17	Solutions. Solubility, Henry's law, colligative properties. Raoult's law.
18	Chemical equilibrium, equilibrium constant. Homogeneous and heterogeneous equilibria. Effect of temperature.
19-20	Rates of chemical reactions. First order rate equation. Effect of temperature, concentration, catalyst. Activation energy, transition state.
21	Acids and bases. Bronsted, Lewis theories, examples. Acidity in aqueous media.
22	Oxidation reduction reactions.
23-26	Chemistry of nonmetallic elements. Survey of systematic aspects of chemical behavior. Stabilities of oxidation states, acid strengths, variations of other properties with atomic number, group, etc.

### Laboratory<sup>8</sup>

The topics in successive laboratory periods are: 1. Physical properties of substances; 2. Empirical formula of a compound (e.g.,  $\text{Sn} \rightarrow \text{SnO}_2$ ); 3. Stoichiometry of a chemical reaction (synthesis of mercuric thiocyanate); 4. Gas laws; 5. Determination of molecular weight of a volatile liquid; 6. Ionization and its chemical consequences; 7. Calorimetry, heat of neutralization; 8. Determination of molecular weight by freezing point depression, oxidation-reduction reactions; 9-10. Chemistry of the nonmetals (2 experiments); 11. Kinetics, reaction rate, reaction order; 12. Voltaic cells, potentiometry; 13. Anion qualitative analysis.

<sup>4</sup> ANDREWS, D. H., AND KOKES, R. J., "Fundamental Chemistry," John Wiley and Sons, Inc., New York, 1962.

<sup>5</sup> BROWN, T. L., "General Chemistry," Charles E. Merill Books, Inc., Columbus, Ohio, 1963.

<sup>6</sup> DRAGO, R. S., AND BROWN, T. L., "Experiments in General Chemistry," Allyn and Bacon, Inc., Boston, 1960.

<sup>7</sup> WASER, J., "Quantitative Chemistry," W. A. Benjamin, Inc., New York, 1961 [Revised ed. published 1964].

<sup>8</sup> Efforts are currently in process to introduce analytical techniques into the first semester laboratory by using procedures which permit good accuracy and precision.

### CHEMISTRY 108, GENERAL CHEMISTRY (Second Semester)

Sessions: 2 lectures, 2 recitations, 6 hours laboratory per week.

Prerequisite: Chemistry 107.

Typical texts: As for Chemistry 107, plus possibly King.<sup>9</sup>

#### Lecture

#### Topic

1-2	Thermodynamics—introduction to second law, Gibbs free energy and equilibrium.
3-9	Equilibrium problems: weak acids and bases, pH; solubility products, common ion effect, hydrolysis, buffers.
10-11	Quantitative analysis: precipitation, adsorption, peptization, titration.
12-15	Electrochemistry: oxidation-reduction, electric cells, Nernst equation.
16-17	Metallic elements. Nature of the metallic state, metallurgical procedures.
18-21	Complex ions, coordination compounds; introduction to crystal field theory.
22-25	Survey of the chemistry of the metals: oxidation states, complexes, metal carbonyls, electronic structures.

Selected topics occasionally included (1 lecture each): silicate minerals, nuclear and radio chemistry, molecular isomerism, stereo-chemistry, electron-deficient bonding.

#### Laboratory<sup>10</sup>

Topics include: use of filter paper and column chromatography; ion-exchange separations (10 weeks); potentiometric experiments (2 weeks); other quantitative work, such as preparation and analysis of complexes (3 weeks).

### CHEMISTRY 234 AND CHEMISTRY 336, ORGANIC CHEMISTRY

Texts: Required, Morrison and Boyd<sup>11</sup>; recommended, Cram and Hammond.<sup>12</sup>

It may be noted that each course is completely self-contained and surveys the entire field of elementary organic chemistry, both aliphatic and aromatic. The first semester course is presumed to have completed such topics as "nomenclature" and "development of the organic chemical vocabulary" in order to leave the second semester course free to concentrate on the chemical aspects of the subject. It is quite possible that the text in either semester may be varied independently of the other, and normally teaching schedules are arranged so that one group of students has one staff member the first semester and a second, whose research interests differ from those of the first as much as possible, for the second semester course. For example, a physical organic chemist might teach the first semester and a natural products chemist the second, or vice versa.

### CHEMISTRY 234

Sessions: 3 lectures, 1 conference, 5 hours laboratory per week.

Prerequisite: Chemistry 108.

#### Lecture

#### Topic

1-2	Covalence and Structure—Atomic orbitals. Bonding. <i>Sigma</i> molecular orbitals. Bond length, bond strength, bond angle. Functional isomerism.
3-4	Saturated Hydrocarbons—Positional isomerism. Conformations. Aliphatic substitution reactions: radicals, chain reactions, mechanisms, transition states. Nomenclature. Functional groups.
5-6	Olefins— <i>Pi</i> molecular orbitals. Stereochemistry. Addition reactions: mechanisms and stereochemistry. Vinyl polymers.

<sup>9</sup> KING, E. J., "Qualitative Analysis and Electrolytic Solutions," Harcourt, Brace and Co., Inc., New York, 1959.

<sup>10</sup> The laboratory program is at present in a development stage, and considerable change is anticipated during the next few years.

<sup>11</sup> MORRISON, R. T., AND BOYD, R. N., "Organic Chemistry," Allyn and Bacon, Inc., Boston, 1959.

<sup>12</sup> CRAM, D. J., AND HAMMOND, G. S., "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1959.

7-8 Dienes—Conjugate addition. Diels-Alder reaction. Rubber-like polymers. Allenes. Acetylenes—Bonding and stereochemistry. Acid reactions. Tautomerism. Petroleum—Fractional distillation. Variety of compounds.

9-12 Aromatic Compounds—Aromatic hydrocarbons. Stability and resonance energy. Electrophilic aromatic substitution: mechanism, influence of substituents on transition state. Carbonium ion rearrangements. Multistep syntheses.

13-14 Alcohols— $S_N1$  and  $E1$  reactions.

15 Phenols—Relative acidities. Nucleophilic aromatic substitution. Quinones.

16-18 Amines—Relative basicities. Diazonium salts. Sulfur compounds—Mercaptans, sulfides, disulfides.

19-22 Stereochemistry—Geometrical and optical isomerism.

23-25 Halides— $S_N2$  and  $E2$  reactions: stereochemistry, variation with structure. Grignard reagents.

26 Ethers—Unreactivity. Epoxides.

27-30 Aldehydes and Ketones—Addition reaction. Aldehyde oxidation reactions. Enolate reactions. Chelation.

31-33 Carbohydrates—Diastereomers, meso compounds. Conformations. Disaccharides, polysaccharides.

34-39 Acids and derivatives, including polyfunctional acids.

40 Amino acids.

#### Laboratory

Text: Fieser.<sup>13</sup>

Experiments currently performed are: melting points (unknown); crystallization (unknown); distillation; extraction; cyclohexene; *n*-butyl bromide; nitrobenzene; aldehydes and ketones (unknown); mandelic acid; adipic acid; acetylsalicylic acid; sulfanilamide; amines (unknown); methyl orange; qualitative organic analysis (2 unknowns); indane-1,3-dione. Total: 16 experiments.

#### CHEMISTRY 336

Sessions: 3 lectures per week.

Prerequisite: Chemistry 234.

<i>Lecture</i>	<i>Topic</i>
1-4	Structure.
5	Reaction mechanisms. Transition state theory.
6-9	Carbonium ions. Hydration of olefins; dehydration of alcohols; etherification; esterification; cationic polymerization, alkyl halides from olefins, alcohols; addition of halogen to multiple linkages; halohydrins.
10-13	Electrophilic aromatic substitution. Nitration; sulfonation; acylation; halogenation; alkylation; reactions of phenols and anilines (nitrosation, coupling, hydrogen exchange, diazotization).
14-17	Molecular rearrangements. Other reactions proceeding through cationic intermediates.
18	Carbanions. Enolates. Keto-enol tautomerism.
19-21	Grignard reagents.
22-23	Addition reactions of aldehydes and ketones.
24	Acetals, urea-formaldehyde polymers, oximes, hydrazones, semicarbazones, bisulfite derivatives, cyanohydrins, benzoin condensation.
25	Active methylene compounds.
26	Hydride reductions. Hydride transfer reactions.
27-29	Nucleophilic displacements: in the aromatic series, at the trigonal carbon atom (polymers from solvolyses), at the saturated carbon atom (elimination reactions).
30	Benzyne chemistry.

<sup>13</sup> FIESER, L. F., "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., San Francisco, 1957.

31 Carbene chemistry.  
 32-35 Reactions of radicals. Peroxide effect, vinyl polymerization, autoxidation, Kolbe electrolysis, halogenation, nitration, acyloin condensation, oxidation, photochemistry.  
 36-39 Molecular reactions: Claisen rearrangement, ester pyrolysis, Diels-Alder reaction.

**CHEMISTRY 342, PHYSICAL CHEMISTRY (First Semester)**

Sessions: 3 lectures per week.

Prerequisite: Chemistry 107, 108; two semesters of general physics with concurrent registration in the third; credit or registration in second semester calculus. Most students have completed the mathematics and physics requirement.

Text: Moore.<sup>14</sup>

<i>Lecture</i>	<i>Topic</i>
1-10	Wave mechanics, properties of fundamental particles.
11-17	Atomic structure.
18-24	Molecular structure.
25-29	Kinetic theory of gases.
30-34	Elementary statistical mechanics.
35-45	Statistical and classical thermodynamics—relation of laws and functions of thermodynamics to behavior of atoms and molecules.

**CHEMISTRY 343, PHYSICAL CHEMISTRY LABORATORY I**

Sessions: 3 hours laboratory per week.

Prerequisite: Chemistry 342.

Text: Shoemaker and Garland.<sup>15</sup>

Philosophy: The laboratory is intended, first, to illustrate principles learned in the lecture course and, second, to give some experience in the use of equipment and techniques capable of precision.

*Typical Set of Experiments*

1. Thermometry: precise calibration of thermistor, thermocouple, or fluid thermometer using the triple point of water and several two-phase transitions. 2. Chemical Equilibrium: constants and the thermodynamic functions for the dimerization of  $\text{NO}_2$  vapor by sickle-gauge determination of pressure of a fixed-volume system as a function of temperature. 3. Two- and Three-Phase Equilibria: a choice of several experiments in this category including construction of a two-component phase diagram through precise freezing point curves monitored by continuous recording, and determination of solvent purities by precise determinations of freezing point curves for a series of synthetically impure solvent samples. 4. The Millikan Oil Drop Experiment: to determine the charge on the electron. 5. The Thompson e/m Experiment: to determine the mass of the electron. 6. Electron Spin Resonance of Free Radicals, with a simple Helmholtz coil system, to determine the magnetogyric ratio of the electron. 7. Vibration-Rotation Spectra of  $\text{HCl}^{35}$ ,  $\text{HCl}^{37}$ ,  $\text{DCl}^{35}$ ,  $\text{DCl}^{37}$  Gas: to determine the internuclear distance, force constant, and interaction parameters. The Boltzmann distribution of populations, as reflected in the distribution of band intensities, is investigated. 8. Atomic Emission Spectra of H and Alkali Metals to verify the theoretical energy levels. 9. Magnetic Susceptibilities of Paramagnetic Salts: bonding schemes. 10. A Variety of the Standard Physical Chemistry Experiments: solution properties, colligative properties, molecular weight determinations, and surface tension; some (but not all) of these are performed by each student.

**CHEMISTRY 344, PHYSICAL CHEMISTRY (Second Semester)**

Sessions: 3 lectures per week.

Prerequisite: Chemistry 342.

Text: Moore.<sup>14</sup>

<sup>14</sup> MOORE, WALTER J., "Physical Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1955.

<sup>15</sup> SHOEMAKER, D. P., AND GARLAND, C. W., "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1962.

<i>Lecture</i>	<i>Topic</i>
1-12	Thermodynamics of phase equilibrium and chemical equilibrium.
13-24	Properties of solutions, nonelectrolytic and electrolytic. Electrochemistry.
25-36	Theories of solid and liquid state methods of crystal structure determination.
37-44	Chemical kinetics; theories and description of experimental methods.

### **CHEMISTRY 345, PHYSICAL CHEMISTRY LABORATORY II**

Sessions: 3 hours laboratory per week.

Prerequisite: Chemistry 343.

This laboratory provides considerable freedom and opportunity for students to do individualistic experiments. Some available experiments follow: 1. A series of electrochemical experiments designed to yield precise thermodynamic data, such as determination of the activity coefficient of HCl over a wide concentration range by e.m.f. measurements, and determination of enthalpies and entropies by temperature coefficient of e.m.f.; 2. The Franck-Hertz experiments: illustration of quantized energy levels and determination of excited-state energies in Hg atoms by inelastic scattering of electrons; 3. Absorption spectroscopy: iodine band system in the visible region; 4. High-resolution emission spectroscopy: Zeeman splittings, isotope shift in the H-spectrum, spin-orbit coupling; 5. Second virial coefficients in gases and gas mixtures: intermolecular interactions; 6. Reaction rates and temperature coefficients: measured by visible, infrared, or ultraviolet absorption, conductance, electron spin resonance, or other methods; 7. Magnetic properties and bonding: electron spin resonance of transition metal ions, nuclear magnetic resonance in a simple apparatus, magnetic susceptibility as a function of temperature to 80° K. to determine the temperature-dependent paramagnetism and magnetic moment, including a study of the singlet-triplet equilibrium in cupric acetate; 8. Lattice energy of solid argon (cf. Expt. 43, Shoemaker and Garland);<sup>15</sup> 9. Dielectric constants and dipole moments of molecules, using the heterodyne beat method; 10. Mass spectrometry: study of species (produced by surface ionization) by means of the von Zahn quarter-quadrupole mass filter; 11. Vacuum techniques: studies of pumping speed (mechanical and diffusion pumping, outgassing, leaks, conductance of tubing, valves, bends, etc.); 12. Raman spectroscopy: molecules such as C<sub>6</sub>H<sub>6</sub>, CC<sub>14</sub> are examined with a rudimentary Raman spectrograph assembled by the students from components (as complete a vibrational analysis as possible is performed); 13. Special projects: some students may spend half the semester in a completely nonstandard special project, often suggested by the student.

### **CHEMISTRY 321, ANALYTICAL CHEMISTRY**

Sessions: 3 lectures, 9 hours laboratory per week.

Prerequisites: 2 semesters of organic chemistry; 1 semester physical chemistry.

Texts: Laitinen,<sup>16</sup> and Meites and Thomas.<sup>17</sup>

<i>Lecture</i>	<i>Topic</i>
1-5	Emission spectroscopy: flame, spark and arc, qualitative and quantitative.
6-7	X-rays: diffraction, absorption, emission.
8-12	Absorption spectrophotometry: visible, ultraviolet, infrared.
13-15	Chemical separations: ion exchange, chromatography, solvent extraction.
16-17	Radiochemistry.
18-21	Ionic equilibria: Debye-Hückel theory.
22-24	pH and acid-base equilibria: aqueous and nonaqueous solvents.
25	Electrode potentials, Nernst equation.
26	Cell e.m.f. and cell reactions.
27	Redox equilibrium and cell e.m.f.

<sup>16</sup> LAITINEN, H. A., "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, 1960.

<sup>17</sup> MEITES, L., AND THOMAS, H. C., "Advanced Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, 1958.

- 28 Potentiometry and titrations.
- 29-30 Conductance and titrations.
- 31-32 Electrolysis and electrolytic separations.
- 33-35 Polarography and amperometry.
- 36-37 Nuclear magnetic resonance spectroscopy.
- 37-38 Mass spectrometry.
- 39-41 Sources of error in chemical analysis: coprecipitation, nonstoichiometric reactions.

**Laboratory**

Sessions: 30 periods of 4½ hours each.

The experiments done in the periods indicated are: 1. Lab orientation, experimental modules; 2. Flame photometry; 3-4. Special problem I; 5-6. Emission spectroscopy, X-ray diffraction (rotation); 7-9. Spectrophotometry (Beer's law, titrations, IR); 10-13. Special problem II; 14-15. Gas chromatography, 16.  $\sigma$ -chemistry (rotation); 16. Equilibrium and salt effects, pH; 17-19. Special problem III; 20. Potentiometric titrations; 21. Polarography; 22-24. Special problem IV; 25-30. Research problem.

**CHEMISTRY 315, INORGANIC CHEMISTRY**

Sessions: 3 lectures per week.

Prerequisite or corequisite: Chemistry 342.

Text: Cotton and Wilkinson.<sup>18</sup> Some topics are covered in more depth than in this text. Frequent reading assignments in the chemical literature are given.

*Lecture* *Topic*

- 1 Wave mechanics.
- 2 Hydrogen atom wave functions, angular momentum.
- 3 Slater orbitals; *aufbau* principle.
- 4 Atomic structures, terms.
- 5 Ionic compounds, ionic radii.
- 6 Lattice energies of ionic crystals.
- 7 Van der Waal's forces, molecular orbital theory.
- 8 Molecular orbital and valence bond theories.
- 9 Hybrid orbitals.
- 10 Examples of application of bonding theories.
- 11 Symmetry theory, electronegativity.
- 12 Hydrogen bond; three-center bonds.
- 13-14 Theories of acids and bases.
- 15 Nonaqueous solvents.
- 16 Magnetic susceptibility.
- 17 Crystal field theory.
- 18 Strong and weak octahedral fields, tetragonal fields.
- 19 Jahn-Teller distortions.
- 20-22 Stereochemistry of coordination compounds.
- 23 Mechanisms of coordination compound reactions.
- 24 Metal carbonyl compounds; metal carbon bonds.
- 25 Aromatic metal compounds.
- 26 Formation constants of complexes.
- 27 The inner transition metal series.
- 28 The chemistry of nonmetals. Group III.
- 29 Group III elements.
- 30-31 Group IV elements.
- 32 Electron deficient compounds.
- 33 Boron hydrides.

<sup>18</sup> COTTON, F. A., AND WILKINSON, G., "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, 1962.

- 34-35 Group V elements.
- 36-37 Group V, VI elements.
- 38-39 Group VII, VIII elements.
- 40-41 Radiochemistry.

### THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY PLAN<sup>19, 20</sup>

The factors motivating change to the present system were basically the same as those at the University of Illinois. There was a strong feeling that each of the four fields—organic, inorganic, physical and analytical—should be taught from the standpoint of the professional specialist with his added insights, enthusiasm, and dedication. This was certainly not possible in the framework of the traditional sequence. The new approach provided much greater opportunities. Organic chemistry was found to be as effectively taught in the second year as it had been in the third, and with the additional advantage that the students felt that they were starting something new and different from either high school or general chemistry. Inorganic, analytical, and physical chemistry can be based on a background of at least two years of college mathematics and physics. Analytical chemistry in particular benefits in being based on prior organic, inorganic, and physical courses. It is at last possible to teach in the introductory analytical course the sort of analytical chemistry which is actually used today. Inorganic chemistry emerges as a professional specialization, distinct from general chemistry, a full year earlier than was possible with the usual system of advanced inorganic courses in the senior year.

The principal differences between the Illinois and the MIT sequences can be seen by comparing the course requirements. There is more early emphasis on physics and mathematics at MIT. The laboratories, in general, are concurrent with, rather than subsequent to, the lecture courses. The required core courses are not completed in three years but extend into the senior year.

Course content is in general similar, but there are certain differences. Instruction in elementary quantitative techniques is not given in the general chemistry course; there is not sufficient laboratory time available in the schedule. Organic identification is required as a separate course, and the third semester of physical chemistry is required instead of being given as a "required elective." The division of analytical into instrumental and noninstrumental is more marked, and there is a greater emphasis on the application of analytical methods to organic systems.

Considerable variation is possible within the general framework of the approach, as has been demonstrated at a number of institutions which have adopted similar plans. The sequence provides not only flexibility but considerable opportunity for saving of time through increased efficiency.

### MASSACHUSETTS INSTITUTE OF TECHNOLOGY COURSE REQUIREMENTS FOR CHEMISTRY MAJORS 1963-1964

#### FIRST YEAR

**FIRST TERM**

- General Chemistry
- Physics I
- Western Civilization
- Calculus I
- Elective

**SECOND TERM**

- General Chemistry
- Physics II
- Western Civilization
- Calculus II
- Elective

#### SECOND YEAR

**FIRST TERM**

- Organic Chemistry I
- Organic Preparations
- Physics III
- Calculus III
- Language
- Humanities

**SECOND TERM**

- Organic Chemistry II
- Organic Preparations
- Physics IV
- Differential Equations
- Humanities

<sup>19</sup> HUME, D. N., *J. Chem. Educ.*, 35, 136 (1958).

<sup>20</sup> *Ibid.*, 37, 335 (1960).

**THIRD YEAR**

**FIRST TERM**

Inorganic Chemistry  
Qualitative Organic Analysis  
Physical Chemistry I  
Physical Chemistry Laboratory  
Humanities  
Elective

**SECOND TERM**

Analytical Chemistry I  
Analytical Laboratory  
Physical Chemistry II  
Physical Chemistry Laboratory  
Humanities  
Elective

**FOURTH YEAR**

**FIRST TERM**

Analytical Chemistry II (Instrumental)  
Instrumental Laboratory  
Physical Chemistry III  
Thesis  
Humanities  
Electives

**SECOND TERM**

Thesis  
Humanities  
Electives

### III. THE BROWN EXPERIMENT<sup>1,2</sup>

LEALLYN B. CLAPP, *Brown University*, Providence, R.I.

According to the "Brown Historical Catalog," the chemistry laboratory was first opened to students in 1853 although lectures in chemistry were given first in 1848. Previous to this natural philosophy was the title of a course which included some medicinal and agricultural chemistry. In 1855, the chemistry course was divided into two parts—inorganic and analytical chemistry. Qualitative and quantitative analysis were listed as separate courses in 1874; organic chemistry was offered in 1889 and physical chemistry for the first time in 1901. In 1930, the first course was entitled general chemistry, a tacit admission that physical chemistry was creeping down to the first course. This historical dating can be duplicated in other universities throughout the country without much variation.

In 1946, when our discussions began on the "Brown Experiment," we categorically denied to ourselves that the historical order of discovery of subject matter was of necessity the order of difficulty in presentation, the logical order of presentation, or the best order for salesmanship of a career.

Why was the curriculum at Brown changed? It was largely due to the dissatisfaction of Paul C. Cross in teaching physical chemistry. He said that he was unable to select subject matter for his course from which the cream had not already been skimmed in previous courses. Physical chemistry had gradually permeated general chemistry, qualitative analysis and quantitative analysis until the formal course in physical chemistry had little new to offer. He did not say that the subject matter had been thoroughly learned, and he was able to present ideas with more thoroughness and rigor, but the freshness of new ideas was replaced by a bolstering of concepts loosely learned. I need only recall the subject of equilibria to remind you how often "physical chemistry" is treated in the first four semesters.

Professor Cross suggested that physical principles should be taught first. We toyed with that idea for a while, but finally gave it up as impractical because the students' background in physics and mathematics was lacking. An alternative was to offer descriptive chemistry in the first year while the student was getting a background in math and physics for the quantitative aspects of chemistry.

The chemistry which we thought was still largely descriptive was that of the elements in the northeast part of the periodic table, what we at Brown call "The Chemistry of the Covalent Bond."

Today we may no longer be justified with these same answers. Students are better prepared in math when they enter now. Organic chemistry, as all sciences must, is going in the direction of quantitative treatment, although it has not arrived yet. However, organic chemists feel that they need a background in equilibrium phenomena and the interpretations available from kinetics before a rigorous year of organic chemistry can be taught. If Morrison and Boyd,<sup>3</sup> and a few other recent textbooks are diagnostic of the state of the union, then some background in physical chemistry is essential for a good presentation of organic chemistry.

In the first year our chemists take three courses in chemistry. One is "The Chemistry of the Covalent Bond." The second is calculus and is taught in the math department, and the third is labelled physics and is also taught elsewhere. However, we try to impress the student with the idea that he is taking three chemistry courses.

In the second year the chemistry curriculum includes a more or less classical year of physical chemistry and a second year of math including differential equations. The text this year is Sheehan, "Physical Chemistry."<sup>4</sup> The laboratory work in the second year includes experiments common to physical chemistry labs in other universities with emphasis on the quantitative aspects. E. F. Greene, who is presently teaching the course, is convinced that laboratory practice in the techniques of quantitative analysis is best taught at the time it is demanded by an experiment. When techniques are taught by a professional analytical chemist just for the sake of technique, we may well ask, "Do the students really know why they are being careful?" The professional analytical chemist may answer that they can learn why later. Professor Greene does not see this necessity. In a kinetics experiment, for example, where the chemist

<sup>1</sup> COLES, J. S., CLAPP, L. B., AND EPPEL, R. P., *J. Chem. Educ.*, 26, 10 (1949).

<sup>2</sup> CLAPP, L. B., *J. Chem. Educ.*, 35, 170 (1958). [Part of a symposium, "New Ideas in the Four-Year Chemistry Curriculum."]

<sup>3</sup> MORRISON, R. T., AND BOYD, R. N., "Organic Chemistry," Allyn and Bacon, Inc., Boston, 1959.

<sup>4</sup> SHEEHAN, W. F., "Physical Chemistry," Allyn and Bacon, Inc., Boston, 1961.

may only hope for an accuracy of 5-10%, does the student need to weigh reactants to four decimal places or use calibrated burets when the reaction is run at ambient temperatures? How best will the student learn that controlling the temperature in a rate study to plus or minus 0.01° may be more significant in an experiment than the error involved in using a triple beam balance to weigh reactants? The argument does not appear to us at Brown to be all on the side of learning analytical techniques for their own values before doing experiments in physical chemistry, although we are aware of the hazards.

The fifth semester of the fundamentals of chemistry is devoted to inorganic chemistry at the level of Gould's text<sup>5</sup> and Jolly's lab manual.<sup>6</sup> In the sixth and seventh semesters, a year of quantitative chemistry, a semester of volumetric and gravimetric methods, and a semester of instrumental methods is required. The inorganic and analytical courses have the benefit of a year of physical chemistry. The treatment of inorganic chemistry does not have to be limited to a descriptive tour of the periodic table, but can be given the rigor it deserves.

The chemistry curriculum is completed with a third course in organic, a third course in physical, a second course in inorganic, and a year of senior research in any of the four fields. Sc.B. degree requirement is 32 semester courses. Chemistry majors must complete 20 courses in the combination chemistry, physics, mathematics, and at least 10 of these courses must be in chemistry. The common pattern is 14 courses in chemistry, 4 in mathematics, and 2 in physics. In the A.B. degree the total is about 16 courses in the three-field combination chemistry, physics, mathematics (one-half of the total college program). Again 10 semester courses in chemistry are required.

In the 15 years we have lived with this curriculum only one major change has been made. This change is included in the above description. During the first four years, 1948-52, the first semester of inorganic chemistry was given concurrently with the second semester of physical chemistry in the second year. Most of our students were also enrolled in differential equations and German. We killed them off with this load, and so we reluctantly moved the inorganic course to the fifth semester and the two analytical courses to the sixth and seventh semesters. This was the lesser of two evils. We would like to have all background courses, including instrumental methods of analysis, completed before the senior research course starts in the fourth year.

What is lost and what is gained by the Brown curriculum?

1. The most important asset is the *initial enthusiasm* with which a student meets a new subject. The first year of college chemistry is not a repetition of high school chemistry. College professors have always recognized the change in the level of sophistication from the high school course. The student at Brown also recognizes it in our curriculum, and this is most important. The text even looks different when it is lying open.

2. Physical chemistry can be taught with all the rigor that the instructor wishes since the students have a year of physics and differential and integral calculus available. Subjects that need repetitious treatment can be dealt with as the instructor finds necessary, and he will know the level of the initial treatment. This lack of faith in the effectiveness of previous courses is a constant hazard in cumulative subject material.

3. Students find the treatment of geometry and structure in general fascinating. It is a good send-off into a career in chemistry.

What have we lost? 1. In dropping qualitative analysis from the laboratory we lost the fascination of unknowns and some of the built-in incentive to work, which is irreplaceable. So far we have not been able to put an unknown into every experiment in the first year. I believe this to be a fault of our own ingenuity rather than the curriculum, but we have not found a good answer to this problem. We have lost the tender loving care of a professional analytical chemist during the early training of the student. Is this irretrievable with this kind of curriculum, or can other faculty members instill the proper respect for the quantitative nature of chemistry?

2. The first year is not a year of organic chemistry. A later course must be used to give an adequate understanding of organic mechanisms, which require some background in physical chemistry. The organic chemist, loyal only to his own field, considers this loss a betrayal of trust. We must consider

<sup>5</sup> GOULD, E. S., "Inorganic Reactions and Structure," Holt, Rinehart and Winston, Inc., New York, 1962.

<sup>6</sup> JOLLY, W. L., "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960.

loyalty to the whole field, however, and my personal view is that organic chemistry does not suffer in the end as much as physical chemistry would from a watered-down presentation in the first year—normally described as general chemistry.

The Brown curriculum is under fire again. This is healthy if for no other reason than that chemical information has doubled since it went into effect. Advanced courses can be changed to meet the discoveries reported in the literature (Peter Yankwich's "trickle-down"). However, a complete turnover in beginning courses every 15 years may be essential.

The present dissatisfaction with the curriculum of the Brown experiment stems from two ideas: 1. that organic chemistry cannot be properly treated without some concepts from physical chemistry, and no part of the course should be entrusted to the first year; and 2. that we are losing potential chemists to math and physics because the first course is descriptive and lacks the rigor to attract the students we would most like to have.

What I would maintain as a result of our 15 years experience is that the "Chemistry of the Covalent Bond" is still an appropriate beginning college course for any student who cannot begin calculus at the time he enters college. It will remain an appropriate beginning course as long as elementary physical chemistry is not a prerequisite for the teaching of organic chemistry.

If science and mathematics are for the young, then we must also entrust the formation of the chemistry curriculum to the young. Older staff members may be better at execution and practical details. The youngest staff members should be the ones who dream up the content. Part of the success of the Brown experiment was due to the fact that all the men involved in the detailed planning were under 35, and the administration fostered a climate in which the experiment could be tried.

A curriculum cannot be pieced together from the four traditional subdivisions and yet maintain integrity to the whole field of chemistry. The curriculum must be built by argument, sifting of subject matter for chaff, and logical timing in the order of presentation. A curriculum can, therefore, not be voted on from alternatives by a large department; it must be arrived at by a hard-fought consent. The losers in a vote will not carry any conviction or enthusiasm to a new curriculum.

## THE BROWN COURSE REQUIREMENTS<sup>7</sup>

### FRESHMAN

#### CHEMISTRY 11, 12: Chemistry of the Covalent Bond.

Sessions: 3 lectures, 1 recitation, 6 hours laboratory per week.

Text: Clapp.<sup>8</sup>

#### PHYSICS 3, 4

Sessions: 3 lectures, 3 hours laboratory per week.

#### MATHEMATICS 8, 9: Calculus.

### SOPHOMORE

#### CHEMISTRY 13, 14: Physical Chemistry.

Sessions: 3 lectures, 4 hours laboratory per week.

Text: Sheehan.<sup>4</sup>

#### MATHEMATICS 29: Calculus and Differential Equations.

#### MATHEMATICS 52: Linear Algebra.

### JUNIOR

#### CHEMISTRY 15: Inorganic Chemistry.

Sessions: 3 lectures, 5 hours laboratory per week.

Text: Cotton and Wilkinson.<sup>9</sup>

<sup>7</sup> The degree requirement is 32 courses for either A.B. or Sc.B. All courses carry 4 semester hours credit, and 4 courses is the semester load. Only physical science courses are listed.

<sup>8</sup> CLAPP, L. B., "Chemistry of the Covalent Bond," W. H. Freeman and Co., San Francisco, 1957.

<sup>9</sup> COTTON, F. A., AND WILKINSON, G., "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, 1962.

**CHEMISTRY 106: Advanced Inorganic**  
Text: Cotton and Wilkinson.<sup>9</sup>

**CHEMISTRY 136: Quantitative Analysis.**  
Sessions: 2 lectures, 8 hours laboratory per week.  
Text: Laitinen.<sup>10</sup>

**CHEMISTRY 145: Identification of Organic Compounds.**  
Sessions: 3 lectures, 10 hours laboratory per week.  
Text: Shriner, Fuson, and Curtin.<sup>11</sup>

#### SENIORS

**CHEMISTRY 137: Instrumental Methods in Quantitative Analysis.**  
Sessions: 2 lectures, 8 hours laboratory per week.  
Text: Strobel.<sup>12</sup>

**CHEMISTRY 97, 98: Senior Research.**

**CHEMISTRY 151: Thermodynamics.**  
Sessions: 3 lectures per week.  
Text: Lewis and Randall.<sup>13</sup>

Other advanced courses are offered in inorganic, organic and physical chemistry.

A.B.'s in Chemistry take Chemistry 11, 12, 13, 14, 15, 136, and three advanced electives. They must complete calculus and physics before taking Chemistry 13, 14. They may delay other parts of the program up to one year.

Sc.B.'s in Chemistry take 20 courses in chemistry, math, and physics, of which 10 must be in chemistry and 4 in math. They must meet prerequisites.

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<sup>10</sup> LAITINEN, H. A., "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, 1960.

<sup>11</sup> SHRINER, R. L., FUSON, R. C., AND CURTIN, D. Y., "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1956.

<sup>12</sup> STROBEL, H. A., "Chemical Instrumentation," Addison-Wesley Publishing Co., Inc., New York, 1960.

<sup>13</sup> LEWIS, G. N., AND RANDALL, M., "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1961.

#### IV. COMBINING FIRST YEAR COLLEGE CHEMISTRY AND PHYSICS FOR STUDENTS MAJORING IN SCIENCE

EDWARD C. FULLER, *Beloit College*, Beloit, Wisconsin

##### INTRODUCTION

Natural science in the past hundred years has developed prodigiously by virtue of specialization. Today, the man-made boundaries between the sciences are disappearing at an accelerating pace. Modern research and modern teaching in science must increasingly utilize interdisciplinary approaches to the discovery of new knowledge and to the transmission of the scientific heritage.

Chemistry has grown to such an extent that it is futile to introduce a student to our science by presenting him with a comprehensive array of facts. The essence of modern chemistry can be perceived by the student only when he comprehends a framework of principles and theories to which facts can be related. Modern theories in chemistry are developing in directions which increasingly demand understanding of certain fundamental physical concepts. The converse is also true: understanding modern physics demands a knowledge of chemistry. Several physical concepts require the student to think in terms of atoms and molecules. Learning some basic chemical concepts along with physics enables the student to grasp more effectively the physical principles involved. The most effective way to present much of basic modern chemistry and physics is to teach them together.

During the past fifteen years, there has been a trend toward moving physical chemistry down from the senior year into the junior or even the sophomore year. Recent general chemistry textbooks are including more physical chemistry and less descriptive inorganic. More and more, chemical phenomena are being interpreted on the basis of fundamental physical concepts. The blending of chemistry with physics is most obvious in studies of the structure of matter and its interactions with energy in the form of heat, electricity, and electromagnetic radiation.

If the beginning student is to understand most readily the fundamental dependence of modern chemistry on physics, he should be introduced to this relationship in an elementary, integrated course. In planning such a course, three questions need to be borne in mind: (1) What special values arise from teaching physics and chemistry together? (2) What subject matter lends itself most effectively to yielding these values? (3) How can combined courses be organized and administered to facilitate the achievement of these values?

The departments of chemistry and of physics in several colleges have developed integrated courses for students majoring in the sciences.<sup>1</sup> This paper is a report about some of them.

##### AREAS OF KNOWLEDGE EASILY INTEGRATED INTO A COMBINED COURSE

The study of classical Newtonian mechanics, which introduces the student to the concepts of force, mass, work, kinetic and potential energy, and a variety of conservation principles, is basic to the entire field of physical science. This foundation enables the student to gain a deeper insight into the kinetic theory of matter. The concepts of work and mechanical energy, of the conversion of mechanical energy into heat, of heat as a mode of motion, and of the relation between temperature and the kinetic energy of molecules help him to interpret the changes in thermal energy accompanying changes of state and chemical transformations. Studying the nature of static and of flowing electricity enables him to understand more clearly the involvement of electric energy in electrolysis and the chemical reactions taking place in galvanic cells. Studying the nature of magnetic and electric fields enables him to comprehend more clearly how charged particles moving in such fields behave and how a study of their motion has led to our contemporary model of atomic structure. Knowledge of atomic structure is prerequisite to understanding contemporary interpretations of the periodic table, the nature of chemical binding, and the relations between particle size and geometric configuration and the chemical properties of atoms, molecules, and ions.

##### PEDAGOGICAL AND PHILOSOPHICAL PROS AND CONS

Exposing students to both physics and chemistry in their first year of college enables them to make a better choice of major. Since several topics (phases of matter, atomic structure, electrochemistry and

<sup>1</sup> During the 1961-1962 academic year, combined physics and chemistry courses were known to be given for science majors at Beloit College, Carleton College, Cornell College (Iowa), Lawrence College, Reed College, the University of Southern Florida, Wabash College, and Whitworth College.

others too numerous to mention) are commonly taught in both physics and chemistry courses, teaching them only once in a combined course saves time for studying other topics. Almost half a semester of chemistry may be gained in a four-semester sequence in physics and chemistry by eliminating duplication. The combined course is especially valuable in the curriculum for preparing students to become secondary school science teachers, since they are often expected to teach both sciences. Alternation between the mathematical approach used in physics and the phenomenological approach more characteristic of chemistry widens the student's outlook on science and how it develops. He learns something about the difference in "style" between the physicist's and the chemist's approach to nature. Students planning to major in chemistry get started in physics at an earlier stage in their education; the converse is true for students of physics. Students with a strong background in chemistry are able to cope with the physics in a combined course more easily than when physics of the same degree of difficulty is encountered in a separate course. Their chemical knowledge "helps them over the humps" in a combined course; the converse is true for students with a strong background in physics. Applying a given concept (e.g., kinetic-molecular theory) to both chemical and physical systems strengthens and deepens a student's understanding of the concept and its usefulness.

Working together in a combined course broadens the outlook of the faculty involved. It is an exhilarating experience to teach such a course. It forces the teacher to choose from among the sacred cows of chemistry and physics the material which is to be included in the integrated course. The rather drastic change of approach engendered by a combined introductory course requires that the faculty think through and revise the whole curriculum for the major. Changes must be made in the course offerings which follow the combined course. Cooperation in the teaching of upper level courses is also encouraged.

Some disadvantages have been encountered in combined courses: postponing a well-motivated student's deep and rapid penetration of physics or chemistry; confusing a poorly prepared student by switching from physics to chemistry and vice versa when sufficient care is not taken to integrate the work; increasing the difficulty of coordinating a student's work in college with what he had in secondary school—particularly if he had "advanced" courses in school; complicating problems of administering the course, since more staff members are involved and need to be consulted when decisions are made on staffing, sectioning for lecture and laboratory groups, scheduling examinations, etc.; the lack of a wide selection of suitable textbooks; the difficulty of "coverage"—the instructor is tempted to select too much subject matter from the wealth of material available. However, those of us who have taught integrated courses feel that these disadvantages are outweighed by the advantages of integration, and I know of no one who plans to return to separate introductory courses.

### SOME SUGGESTIONS ON COURSE CONTENT

*Basic topics:* measurements, units, mathematical techniques; Newtonian mechanics; conservation of momentum, mass-energy, electric charge; heat and kinetic-molecular theory of matter; fields of force; electrical nature of matter and atomic structure (including the quantized nature of electromagnetic radiation and electron energy levels); mass relations in chemical reactions; chemical elements and atomic masses; classification of elements and compounds; the periodic table; chemical binding and structure of simple molecules; rates of reaction; chemical equilibrium.

*Peripheral topics:* wave motion, radioactivity and nucleonics; entropy, enthalpy, free energy and the second law of thermodynamics; colligative properties; ions in solution, electrochemistry.

### SCOPE OF AN INTEGRATED COURSE

No one should attempt to teach in a one-year course all of the content suggested above. Depth of understanding is much more important than breadth of coverage. The teaching scientist must always make plain to his students that some models, concepts, and theories may be ephemeral; today's best explanation of nature's behavior may well be passé tomorrow. He must also make it clear that science does not explain all. We have to live in ignorance of the explanations of some phenomena we should very much like to understand. The contemporary state of science should not be presented as a "slick" explanation of nature. It is a rough-hewn construct created with infinite patience and care, but, nevertheless, possessing many ragged edges.

In some combined courses calculus is used in presenting physical concepts. In others, graphical approaches are employed, using the tangent to a curve as representing the instantaneous value for a rate of change, and measuring the area under a curve in lieu of integration. The proponents of calculus feel that the physical meaning of a derivative and of an integral is important to the beginning student. One way of gearing the mathematics used to the sophistication of the students may be to teach the combined course without calculus, and to include calculus extensively in subsequent courses. Another way of meeting the students' needs is to teach the elements of calculus along with the physics.

Some courses include discussions of the historical and philosophical development of scientific concepts, but this approach is likely to be confined to one or two "case histories." Though teachers of integrated courses agree that it is important for students to grasp "the spirit of science," "the scientific attitude," or "the scientific habit of thought," they have not found any one best way for achieving these subtle understandings. Sometimes the selection of a broad theme to be threaded through the course helps to focus students' attention on the scientific process. Some themes which have been suggested are: (1) Transformations of Matter and Energy; (2) Developing a Model of the Universe; (3) The Periodic Table of the Elements; (4) The Structure of Matter; (5) Particles and Atomicity; and (6) Change and Invariance. Great syntheses of ideas may also be useful for giving coherence to a combined course. Some of these are: (1) The Newtonian Synthesis (force, mass, motion, momentum, energy, conservation, and relativity); (2) Fields (gravitational, electric, magnetic, and nuclear); (3) Elements and Chemical Change (composition, structure, and energy); (4) Thermodynamics (statistical mechanics, heat, and kinetic theory); and (5) Change (as a continuous gradual process and as a discontinuous or quantized process).

In choosing topics to be included in a combined course it is obvious that there is no one most desirable selection. A variety of approaches in different colleges is preferable to a universal pattern. With any pattern, however, considerable effort must be devoted to really integrating the physics and chemistry—not just teaching a segment of one and then a segment of the other.

## LABORATORY WORK

Some aims of laboratory instruction are: to pose a series of problems which a student can solve, albeit imperfectly; to promote the interconnection of data, results, concepts, and previous experience; to provide practice in accurate and reliable recording of data; to raise as well as to answer questions; to interconnect physics and chemistry; to develop intellectual honesty rather than to foster the search for the "right" answers; to inculcate the scientific attitude; to train the student to analyze errors, and to learn how to minimize them by appropriate modifications in experimental procedures; to see the limitations of a given experimental method, and to learn how such limitations may be overcome; to confront the student with physical experience corresponding to concepts expounded in the classroom; to demonstrate the extension of human sensory perception by appropriate instruments; and to force the student to make decisions and judgments, and to differentiate between relevant and irrelevant data.

The most important function of laboratory work is to lay bare the methodology of the science and to require a logical interpretation for a given cluster of phenomena. It is valuable for the student occasionally to be confronted by problems which he must attack without complete and detailed directions from the teacher. When he stumbles and recovers (with more or less aid from the teacher) he will be experiencing the frustrations and triumphs of scientific investigation in a very personal way.

Techniques of teaching which implement these aims include: designing experiments which lead to results the student does not anticipate; providing progressively less detailed directions as the student gains experience; giving conventional experiments an unconventional twist; using "unknowns"; presenting the limited but useful aspects of "black box" instruments; using some laboratory experiments which "stand on their own feet," i.e., are not dependent on materials discussed in the classroom; using "open-ended" experiments; and using simple rather than complex apparatus to concentrate the student's attention on ideas rather than on manipulation. Whenever possible, experiments should be multipurpose, e.g., using a potentiometer to measure the e.m.f. of a series of galvanic cells prepared by the student, rather than any miscellaneous assortment of ready-made cells.

The spirit of science cannot be imparted by words alone. The nature of the scientific enterprise is shown most clearly by carefully thought-out laboratory work. It is better for the student to perform a

few experiments well than to do many hastily. "Fill-in-the-blank" reports are much less valuable than keeping a notebook or journal or writing reports in the style of articles for scientific periodicals. The most important function of a laboratory report is to focus the student's attention on the interpretation of data and the significance of results obtained from the experiment.

Concepts which may well be studied in the physics-chemistry laboratory include: density and specific gravity, gas laws, Faraday's laws of electrolysis, e.m.f. of galvanic cells, constant composition of a compound, types of chemical reactions, molecular mass from freezing point depression of a solvent, rates of reaction, chemical equilibrium, ionization constants and pH, oxidation-reduction titrations, practice and precision of measurement, conservation of energy and momentum, free fall, graphical composition of forces, Lenz's law, electric circuits, wave motion, calorimetry, and simple potentiometry.

## PATTERNS OF INSTRUCTION

Several different ways of staffing combined courses have been used. These range from having one person (a physicist or a chemist) do all the classroom teaching for a given group of students to using a physicist to teach the physics in the classroom and in the laboratory and a chemist for the chemistry in each case. Using a physicist for physics lectures, a chemist for chemistry lectures, and one person (a physicist or a chemist) for recitation sections is an intermediate pattern. For a chemist or a physicist to be the only person involved in both lecture *and* laboratory instruction for two semesters of a combined course puts a considerable burden on him. When several textbooks combining physics and chemistry for use in integrated courses become available, this burden will be considerably lightened. The general pattern of using a physics text and a chemistry text supplemented generously with mimeographed notes does not seem to confuse the students inordinately, but a single textbook would certainly be better. The staffs of almost all of the colleges offering an integrated course have prepared their own laboratory manuals.

## COURSES WHICH FOLLOW THE INTEGRATED COURSE

The nature of "follow-up" courses will, of course, depend upon the objectives of a given department of chemistry or physics. Such courses may be designed to provide continuity in the curriculum for a departmental major or minor, or to be terminal for work in that department. Generally, a student takes a semester course in physics with topics selected so that completing the combined course and the one-semester supplement is essentially equivalent to taking a two-semester course in general college physics. In some cases, students embark immediately on typical physics courses at the intermediate level after completing the combined course.

In chemistry the situation is much the same. A student may take a semester course in chemistry (frequently including qualitative analysis) which gives him the equivalent of a year course in general chemistry, when it follows the combined course. An alternative arrangement is to have the student proceed with fairly typical courses in quantitative analysis or organic chemistry after completing the two-semester combined course. In some cases, courses in thermodynamics and in atomic physics, adapted to the needs of students majoring in physics or in chemistry, have grown out of the experience of physicists and chemists working together in the elementary course. These courses, however, are usually staffed by one man—a physicist or a chemist.

## CURRENT INTEREST IN COMBINED COURSES

A report on the teaching of physics and chemistry in a combined course was sent to chairman of physics and chemistry departments in four-year colleges and junior colleges.<sup>2</sup> In addition to this general mailing, reports have been sent to 537 persons who wrote to request copies. These special requests have come from 43 states and 15 foreign countries. Of the 537 requests, 193 came from chemistry teachers, 86 from physics teachers, 127 from teachers and administrators interested in science education in general, 53 from high school teachers and administrators, and 78 from publishing houses, research institutes, industrial scientists, etc.

<sup>2</sup> "Report of the Beloit Conference on Teaching Physics and Chemistry in a Combined Course," December 1961 (available through Edward C. Fuller or Ronald Palmer, Beloit College, Beloit, Wisconsin).

So far as the writer knows, no college which has developed a course combining physics and chemistry for students majoring in science has reverted to separate elementary courses. The continuing interest of others, reflected in the inquiries noted above, leads the writer to believe that the years ahead will witness the establishment of many new courses combining elementary college physics and chemistry.

## SEQUENCE OF COURSES IN SCIENCE AND MATHEMATICS FOR CHEMISTRY MAJORS (1963-1964)

### FIRST YEAR

FALL: Physics-Chemistry 101; Calculus  
SPRING: Physics-Chemistry 102; Calculus

### SECOND YEAR

FALL: Physics; Organic Chemistry I  
SPRING: Qualitative and Quantitative Analysis; Organic Chemistry II

### THIRD YEAR

FALL: Physical Chemistry I  
SPRING: Physical Chemistry II

### FOURTH YEAR

FALL: Inorganic; Advanced Chemistry; Senior Research  
SPRING: Instrumental Methods; Advanced Chemistry; Senior Research

## COURSE CONTENT OUTLINE BASIC CONCEPTS IN PHYSICS AND CHEMISTRY

### Physics-Chemistry 101, 102

#### *Lecture Topics*

<b>1. THE INTERDEPENDENCE OF MODERN CHEMISTRY AND PHYSICS</b>	<b>3. MOTION OF A PARTICLE</b>
<b>2. FUNDAMENTAL MEASUREMENTS</b>	3.1 Relativity of motion 3.2 Uniform motion in a straight line 3.3 Relative velocities 3.4 Instantaneous speed and velocity 3.5 Acceleration 3.6 Straight-line motion with constant acceleration 3.7 Freely falling bodies 3.8 Motion of a projectile
2.1 Length 2.2 Time 2.3 Mass 2.4 Force 2.5 Position 2.6 Displacement 2.7 Scalars and vectors	

#### 4. FORCE AND MOTION

- 4.1 Starting and stopping motion
- 4.2 Newton's first law of motion
- 4.3 Newton's second law of motion
- 4.4 Forces in equilibrium
- 4.5 Newton's third law of motion
- 4.6 Absolute systems of units
- 4.7 Weight and mass
- 4.8 Pairs of forces and Newton's third law
- 4.9 Momentum
- 4.10 Conservation of momentum
- 4.11 Impulse

#### 5. WORK AND ENERGY

- 5.1 Work done by forces
- 5.2 Units for expressing work
- 5.3 Scalar product of two vectors
- 5.4 Relation between work and energy
- 5.5 Kinetic energy
- 5.6 Potential energy in a uniform gravitational field
- 5.7 Conservation of mechanical energy
- 5.8 Kinetic and potential energy transformations
- 5.9 Power
- 5.10 Elastic and inelastic impact

#### 6. HEAT AND WORK

- 6.1 The nature of heat
- 6.2 Units of heat
- 6.3 Calorimetry
- 6.4 Work and heat
- 6.5 First law of thermodynamics

#### 7. LIQUIDS

- 7.1 Three phases of matter
- 7.2 Pressure
- 7.3 Density and specific gravity
- 7.4 Pressure due to weight of a liquid
- 7.5 Pressure in a confined liquid
- 7.6 Atmospheric pressure
- 7.7 Manometers
- 7.8 Archimedes' principle

#### 8. GASES

- 8.1 The nature of gases
- 8.2 Effect of pressure on gas volume
- 8.3 Effect of heating on gas volume
- 8.4 Temperature and its measurement
- 8.5 The ideal gas law
- 8.6 The kinetic-molecular theory of gases
- 8.7 Partial pressures in mixtures of gases
- 8.8 Real *vs.* ideal gases

#### 9. SOLIDS: PHYSICAL CHANGE IN SYSTEMS OF MATTER

- 9.1 The nature of solids
- 9.2 Heat and changes of phase
- 9.3 Temperature and changes of phase
- 9.4 Gas-liquid equilibria
- 9.5 Solid-liquid equilibria
- 9.6 Gas-solid equilibria
- 9.7 Systems in physical equilibrium; phase diagrams

#### 10. CHEMICAL CHANGE IN SYSTEMS OF MATTER

- 10.1 The meaning of chemical change
- 10.2 Mass relations in chemical reactions
- 10.3 The atomic concept of matter
- 10.4 Relative atomic masses
- 10.5 The concept of the mole
- 10.6 Chemical formulas
- 10.7 Chemical equations
- 10.8 Volume relations in chemical reactions
- 10.9 Avogadro's principle
- 10.10 Molar volume and molecular masses

#### 11. HEAT, WORK, AND PHYSICAL CHANGES; PHYSICAL THERMODYNAMICS

- 11.1 Thermodynamic variables in a system
- 11.2 Heat and internal energy; the first law of thermodynamics
- 11.3 Heat and work of expansion at constant pressure
- 11.4 Enthalpy
- 11.5 Thermodynamics of ideal gases

#### 12. HEAT, WORK, AND CHEMICAL CHANGES; CHEMICAL THERMODYNAMICS

- 12.1 Thermochemistry; Hess's law
- 12.2 Heats of reaction at constant volume and constant pressure
- 12.3 Heats of formation of compounds
- 12.4 Energy changes in spontaneous processes

#### 13. SPONTANEOUS PROCESSES

- 13.1 Entropy
- 13.2 Entropy changes in spontaneous processes; second law of thermodynamics
- 13.3 Free energy
- 13.4 Free energy changes in spontaneous processes

**14. SYSTEMS AT EQUILIBRIUM**

- 14.1 Static and dynamic equilibrium
- 14.2 Equilibria in the system, water
- 14.3 Equilibrium in the system,  $H_2$  -  $I_2$  -  $HI$
- 14.4 The law of mass action and the equilibrium constant
- 14.5 Free energy and equilibrium constant

**15. ELECTROSTATICS**

- 15.1 Electrified bodies
- 15.2 Charging by induction
- 15.3 Electroscopes
- 15.4 Forces between charges; Coulomb's law
- 15.5 c.g.s. and rationalized m.k.s. units
- 15.6 Conservation of charge

**16. ELECTRIC FIELDS**

- 16.1 Field intensity
- 16.2 Fields from point charges
- 16.3 Lines of force
- 16.4 Electrostatic shielding

**17. ELECTRIC POTENTIAL**

- 17.1 Potential difference
- 17.2 Potential due to a point charge
- 17.3 Equipotential surfaces
- 17.4 Potential gradient

**18. ELECTRIC CAPACITANCE**

- 18.1 Capacitance of a sphere in vacuum
- 18.2 Capacitors
- 18.3 Energy of a charged capacitor

**19. FLOW OF ELECTRICITY IN METALLIC CONDUCTORS**

- 19.1 Current
- 19.2 Current density
- 19.3 Ohm's law
- 19.4 Electric energy
- 19.5 Resistivity
- 19.6 Electromotive force
- 19.7 Direct current circuits
- 19.8 Voltmeters and ammeters
- 19.9 The potentiometer

**20. FLOW OF ELECTRICITY IN LIQUIDS**

- 20.1 Electrolytes and nonelectrolytes
- 20.2 Colligative properties of nonelectrolytes
- 20.3 Colligative properties of electrolytes
- 20.4 Ionic theory of electrolytic conduction

**21. CHEMICAL CHANGES PRODUCED BY ELECTRIC CURRENTS; ELECTROLYTIC CELLS**

- 21.1 Strong and weak electrolytes
- 21.2 Arrhenius theory for weak electrolytes
- 21.3 Debye-Hückel theory for strong electrolytes
- 21.4 Acids, bases, and salts
- 21.5 Electrolytic reactions
- 21.6 Faraday's laws of electrolysis

**22. ELECTRIC CURRENTS PRODUCED BY CHEMICAL CHANGES; GALVANIC CELLS**

- 22.1 The Daniell cell; oxidation-reduction
- 22.2 Types of half-cells
- 22.3 Fuel cells
- 22.4 Electrode potentials
- 22.5 Standard oxidation potentials
- 22.6 e.m.f. as a measure of system reactivity

**23. THERMODYNAMICS OF ELECTROCHEMICAL CELLS**

- 23.1 The Nernst equation—single electrode
- 23.2 The Nernst equation—galvanic cell
- 23.3 Standard oxidation potentials and the equilibrium constant for a reaction
- 23.4 Electric energy from galvanic cells
- 23.5 e.m.f. and free energy in a cell
- 23.6 Free energy and spontaneity in a cell reaction
- 23.7 Uses of e.m.f measurements

**24. MAGNETIC FIELDS**

- 24.1 Magnets
- 24.2 Forces between magnetic poles; Coulomb's law
- 24.3 Field intensity
- 24.4 Magnetic moment
- 24.5 Terrestrial magnetism

**25. MAGNETIC FIELDS PRODUCED BY ELECTRIC CURRENTS**

- 25.1 Field produced by a current in a straight wire, in a loop, and in a helix
- 25.2 Field intensity around a wire carrying a current
- 25.3 Field intensity generated by a current element
- 25.4 Field intensity in a circular coil
- 25.5 Field intensity produced by a long straight wire
- 25.6 Equivalence of a moving charge and a current

## 26. FORCES ON CHARGES MOVING IN MAGNETIC FIELDS

- 26.1 A charge moving in a magnetic field
- 26.2 A charged particle moving in an electromagnetic field
- 26.3 A wire carrying a current
- 26.4 Torque on a coil carrying a current; galvanometers
- 26.5 Force between two parallel conductors

## 27. ELECTROMAGNETIC INDUCTION

- 27.1 Motion of a wire carrying a current in a magnetic field
- 27.2 Magnetic flux density
- 27.3 Faraday's law of electromagnetic induction
- 27.4 Lenz's law
- 27.5 Electric generators

## 28. CIRCULAR MOTION

- 28.1 Angular displacement, speed, velocity
- 28.2 Angular speed, linear speed, angular acceleration
- 28.3 Equations of motion for constant angular acceleration
- 28.4 Uniform circular motion
- 28.5 Centripetal acceleration
- 28.6 Centripetal and centrifugal forces
- 28.7 Path of a charged particle moving across a uniform magnetic field
- 28.8 Periodicity of uniform circular motion
- 28.9 Planetary motion
- 28.10 Newton's law of universal gravitation
- 28.11 The gravitational field
- 28.12 The curvature of space

## 29. PERIODIC MOTION

- 29.1 Introduction
- 29.2 Simple harmonic motion
- 29.3 The reference circle

## 30. WAVE MOTION

- 30.1 Vibrating bodies and wave motion
- 30.2 Equation of wave propagation
- 30.3 Huygens' principle
- 30.4 Standing waves
- 30.5 Transverse waves
- 30.6 Longitudinal waves

## 31. SOUND WAVES

- 31.1 The nature of sound
- 31.2 Frequency and pitch
- 31.3 Resonance
- 31.4 Doppler effect
- 31.5 Quality and harmonics
- 31.6 Vibration of strings
- 31.7 Vibrating air columns

## 32. LIGHT WAVES

- 32.1 Electromagnetic radiation
- 32.2 Electromagnetic spectrum
- 32.3 Speed of light
- 32.4 Reflection and refraction of light
- 32.5 Reflection and refraction of waves
- 32.6 Refraction effects
- 32.7 Critical angle; total reflection
- 32.8 Refraction and dispersion
- 32.9 Interference
- 32.10 Diffraction
- 32.11 The diffraction grating

## 33. THE FUNDAMENTAL PARTICLES OF MATTER

- 33.1 Conduction of electricity through gases
- 33.2 Cathode rays
- 33.3 The electron
- 33.4 Positive rays, gaseous ions, the proton
- 33.5 Radioactivity
- 33.6 The nuclear atom
- 33.7 The neutron; isotopes

## 34. QUANTUM THEORY; ATOMIC STRUCTURE

- 34.1 The concept of quantization
- 34.2 Optical and X-ray spectra
- 34.3 The Bohr theory; hydrogen atom
- 34.4 Modification of Bohr theory for more complex atoms
- 34.5 Quantum numbers—their significance
- 34.6 Electron configurations of the elements

## 35. THE WAVE-MECHANICAL CONCEPT OF THE ATOM

- 35.1 Wave-particle duality
- 35.2 De Broglie's hypothesis
- 35.3 Schrödinger's wave equation
- 35.4 Orbitals *vs.* orbits
- 35.5 The spatial distribution of electronic charges with different quantum numbers

## *Lecture Topics*

**36. ATOMIC STRUCTURE AND THE PERIODIC TABLE OF THE ELEMENTS**

- 36.1 Periodicity in chemical properties; families of elements
- 36.2 Mendeléeff's periodic table
- 36.3 Atomic number and atomic mass
- 36.4 Periodicity in physical properties
- 36.5 The extended periodic chart and quantum numbers for valence electrons

**37. CLASSIFICATION OF PURE SUBSTANCES**

- 37.1 Classes of elements
- 37.2 Classes of compounds

**38. CHEMICAL BINDING IN IONIC COMPOUNDS**

- 38.1 The crystal lattice and unit cell
- 38.2 Ions in lattices
- 38.3 Energy of formation of ionic bonds
- 38.4 Electron affinity—Born-Haber cycle
- 38.5 The octet rule
- 38.6 Properties of ionic compounds explained by ionic binding

**39. CHEMICAL BINDING IN COVALENT COMPOUNDS WITH ONLY SINGLE BONDS**

- 39.1 Alternative models: atomic orbital overlaps, molecular orbitals, charge cloud repulsion
- 39.2 Diatomic molecules—one element
- 39.3 Diatomic molecules—two elements
- 39.4 Triatomic molecules—two elements
- 39.5 Tetraatomic molecules—two or more elements

**40. HYBRIDIZED ORBITALS IN COVALENT COMPOUNDS**

- 40.1 The nature of hybridization
- 40.2 Hybrids of two orbitals
- 40.3 Hybrids of three orbitals
- 40.4 Hybrids of four orbitals
- 40.5 The octet rule

**41. BOND POLARITY AND ELECTRONEGATIVITY**

- 41.1 Dipole moment and dielectric constant
- 41.2 Partial ionic character of covalent bonds
- 41.3 Comparative electronegativities

**42. MULTIPLE BONDS BETWEEN ATOMS**

- 42.1 *Pi* binding in double bonds
- 42.2 *Cis-trans* isomerism
- 42.3 *Pi* binding in triple bonds
- 42.4 Resonance and delocalized electrons
- 42.5 Binding within some polyatomic ions

**43. BINDING OTHER THAN IONIC AND COVALENT**

- 43.1 Dipole interactions
- 43.2 The hydrogen bond
- 43.3 The metallic bond

**44. MACROMOLECULES**

- 44.1 Ionic crystals
- 44.2 Covalent crystals
- 44.3 Metallic crystals
- 44.4 Noncrystalline polymers

**45. BOND ENERGIES**

- 45.1 Covalent bond energies from thermochemical equations
- 45.2 The process of solution
- 45.3 Comparative strengths of electrolytes

**46. RATES AND MECHANISMS OF REACTIONS**

- 46.1 Breaking and making bonds
- 46.2 Energy of activation; catalysis
- 46.3 Effect of increasing temperature
- 46.4 Effect of increasing concentration
- 46.5 Collision theory of reaction
- 46.6 Transition state theory
- 46.7 Complex reactions
- 46.8 Heterogeneous reactions

**47. REACTIONS OF ATOMIC NUCLEI**

- 47.1 The equivalence of matter and energy
- 47.2 The characteristics of radioactivity
- 47.3 The binding between nuclear particles
- 47.4 Nuclear interactions in particle accelerators
- 47.5 Nuclear fission
- 47.6 Nuclear fusion

*Laboratory Experiments, 1963-1964*

**FIRST SEMESTER**

1. Accuracy in Laboratory Measurements; The Period of a Simple Pendulum
2. Relation among Variables: P, V, t, and M in Gases
3. Forces as Vectors
4. Thermochemical Measurements: Heat of Neutralization; Heat of Solution
5. Free Fall; Acceleration
6. Atomic Mass of a Metal
7. Conservation of Momentum
8. Electrical Conductivity of Pure Liquids and Solutions
9. Conservation of Energy: Determination of the Mechanical Equivalent of Heat
10. Electrolytic Determination of Atomic Mass and Avogadro's Number
11. Electrical Potential Difference
12. Converting Chemical into Electrical Energy
13. Electric Fields

**SECOND SEMESTER**

1. Electrical Resistance
2. Relative Chemical Reactivity by Displacement Reactions
3. The Tangent Galvanometer
4. Oxygen and Oxides
5. Standing Waves
6. The Halogens
7. The Diffraction Grating
8. Ionic and Covalent Bonding
9. Interference of Light: Young's Double Slit Experiment
10. The Rate of Chemical Reaction
11. The Geiger Counter and Scaler
12. Chemical Equilibrium
13. The Half-Life of Radioactive Silver

## V. THE EARLHAM CHEMISTRY CURRICULUM<sup>1,2</sup>

GERALD R. BAKKER, O. THEODOR BENFEY, WILMER J. STRATTON, and LAURENCE E. STRONG

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For the past seven years the Earlham chemistry faculty has been puzzling over the problem of developing an effective presentation of chemistry to undergraduates. A preliminary plan was proposed in 1958. The essential feature of the proposal for a four-year curriculum was that a sequence of courses should be based on the major concepts that currently provide the conceptual structure of chemistry.

The usual chemistry curriculum is based not so much on conceptual patterns as it is on certain technical skills, exemplified by analytical procedures, or on arbitrary classification schemes which embody such dichotomies as organic versus inorganic. Fortunately, chemists have been able to move a considerable distance toward a unified view of chemical reactions based on principles of electrostatics and mechanics. The problem was to find a usable conceptual framework on which a curriculum could be built.

The first step toward developing a curriculum must be to recognize that there is no agreed upon rationale or theory of learning to guide the organization of a sequence of courses. Whatever may be said about chemistry as a science, it is certainly true that developing a chemistry curriculum is fundamentally an empirical procedure. It is, therefore, in a spirit of curricular empiricism that the present set of chemistry courses has been developed.

In place of courses covering the traditional subject matter subdivisions, each course has been designed to focus on one or a few major concepts. Around these concepts descriptive material is presented, either illustrating the usefulness of the concepts or their limitations.

The outline of the curriculum is shown below and detailed course descriptions are appended. In keeping with our philosophy of curriculum development, we prefer to avoid detailed comparisons between our program and the usual four-year program. Such comparisons tend to obscure the point of what we are trying to do. However, a few points of comparison between the Earlham program and a standard curriculum may be useful.

Much of the material from the usual organic chemistry course now appears in two courses, one in the first, the other in the third year. The usual material of a physical chemistry course is spread over courses in all four years. There is no formal course in analytical chemistry; the most rigorous presentation of analytical techniques occurs in the winter term of the sophomore year, but analytical work is made a part of almost every course, emphasizing thereby the importance of precision measurements for any investigation of a chemical system.

By subdividing chemistry into areas with conceptual coherence, we believe that we are conveying to the students, far more successfully than in our earlier curriculum, a feeling for the structure of the subject. Evidence is accumulating that a student is more likely to be stimulated to pursue a subject on his own if he catches on to the conceptual structure of his discipline. By becoming aware of this structure he can handle problems encountered outside the classroom with some assurance of success.

### COURSE SEQUENCES

Earlham College operates on a 3-term academic calendar, with 3 courses per term. With this calendar, every term-course carries the same credit, equivalent to  $3\frac{1}{3}$  semester credit hours.

Three paths are available in the chemistry curriculum.

<sup>1</sup> STRONG, L. E., AND BENFEY, O. T., *J. Chem. Educ.*, 35, 164-167 (1958).

<sup>2</sup> BAKKER, G. R., BENFEY, O. T., STRATTON, W. J., AND STRONG, L. E., *J. Chem. Educ.*, 41, 188-185 (1964).

A) The basic program for a chemistry major is given in the following table in which the numbers are the chemistry course numbers from the college catalog:

	FALL	WINTER	SPRING
FRESHMAN:	11. Particles of Chemistry	12. States of Matter	13. Covalent Bond
SOPHOMORE:		46. Ions	50. Chemical Energy
JUNIOR:	51. Resonance and Aromaticity	52. Kinetics and Mechanisms	53. Biochemistry
SENIOR:	54. Thermodynamics	80. Seminar	85. Independent Study <sup>3</sup>
	55. Structure and Periodicity		

B) For students with a good mathematics background and a good high school chemistry course, an alternative sequence is offered:

	FALL	WINTER	SPRING
FRESHMAN:	Accelerated Mathematics	Physics (Mechanics)	States of Matter (Special section)
SOPHOMORE:	Covalent Bond (Special section)	46. Ions	50. Energy
JUNIOR	As in basic sequence above.		
SENIOR			

Students who successfully complete the accelerated mathematics course with a grade of *B* or better receive two terms of credit in mathematics. Similarly, two terms of credit in chemistry is given those who satisfactorily complete the special "States of Matter" course. The latter course is intended to bring participating students in one term to the level of achievement reached in the basic program at the end of two terms of chemistry. Some topics, however, are postponed to the special fall-term "Covalent Bond" course, which is limited to students in the mathematics-physics-chemistry sequence. At the end of both covalent bond courses, the two programs merge, all continuing students taking the same course, Chemistry 46, "Ions."

C) For students whose mathematics background does not qualify them for the mathematics-physics-chemistry sequence, but who have an excellent high school chemistry background in both class and laboratory work, a third entry into the chemistry curriculum is possible. This consists of exemption from Chemistry 11, and sometimes from Chemistry 12, and enrollment in the next course of the basic program. An increasing number of students with a good record in high school CBA<sup>4</sup> or CHEM Study<sup>5</sup> courses are likely to follow this path.

Chemistry majors intending to go on to graduate work take all chemistry courses with the exception that "Biochemistry" is optional. The *minimum* major requirement is completion of all courses through "Reaction Kinetics and Mechanisms," plus "Seminar" and "Independent Study."

Students majoring in chemistry are expected to complete at least two terms of calculus and three terms of physics. Those planning to continue their study in graduate school are encouraged to continue mathematics through differential equations and advanced calculus. For these latter students more physics is recommended as is the acquisition of a reading knowledge of German. Some calculus is used in Chemistry 50 and considerably more in Chemistry 52 and 54. Library reading in German is necessary for Chemistry 51.

Premedical students not majoring in chemistry take chemistry courses through "Ions," plus the course "Resonance and Aromaticity." "Biochemistry" is taken by many. The course, "Chemical Energy," is recommended by the Biology Department for its majors.

## LABORATORY WORK

The aim of our laboratory program is to involve the student in scientific inquiry of a kind requiring the use of both experiment and theory in the solution of a problem. The student needs to work on problems that are to him genuine and that challenge him intellectually. He must be involved in the design of experiments, and must develop skill in interpreting the data he obtains.

<sup>3</sup> The "Independent Study" course is often taken in the summer as part of a research participation program.

<sup>4</sup> CHEMICAL BOND APPROACH PROJECT, "Chemical Systems," McGraw-Hill Book Co., Inc., New York, 1964.

<sup>5</sup> CHEMICAL EDUCATION MATERIAL STUDY, PIMENTEL, G. C., Ed., "Chemistry: An Experimental Science," W. H. Freeman and Co., San Francisco, 1963.

We feel that we have only begun to build a laboratory program which satisfies the above criteria. We have found, however, that suitable problems arise most often out of previous classroom or laboratory work. There are a number of promising leads which we are following. In the first-year program the method of continuous variation is a powerful tool for studying not only the stoichiometry of a variety of reactions, but also the various changes which are associated with and signify chemical change. With this method, it is possible to display a chemical system in a way that gives a more realistic view than the idealized equations so commonly used as the only presentation. When the method of continuous variation is applied to real chemical systems, many questions are raised, not all of which have ready answers in the existing literature.

Energy measurements have also proved useful for studies in the first-year laboratory. Simple calorimetry can be introduced early, using inexpensive thermometers and insulated plastic beakers.

In the second year, analytical work can be most stimulating when applied, not to artificial unknowns, but to such areas as equilibrium studies and empirical formula determinations. We find that these studies often evolve into minor research problems and generate considerable student interest.

## TEXTBOOKS

Teachers are often reluctant to reorganize a course until a suitable textbook is available. However, using a text that does not completely fit the course, or using several texts (such as the new chemistry paperbacks), or even no text at all, can have advantages. Both teachers and students are forced to approach the material in a more independent fashion; they are more critical of what they read and less dependent on "what the book says." It is then only a small step from the use of multiple secondary sources to the use of the original literature.

Use of the chemical literature is, in addition, fostered by assigning readings from journal articles, designing experiments which require the use of the original literature, and requiring term papers not neatly covered in texts or secondary sources. Another reason for encouraging and even demanding that students become acquainted with the chemical literature is the tremendous bulk of published information. No course nor any curriculum deals with more than a minute fraction of the available descriptive chemistry. Students must see something of the scope of factual information, and the best place for them to see it is in the library.

## TEACHING STAFF

Present faculty members most responsible for the different courses are: (1) Particles of Chemistry: Gerald R. Bakker and Laurence E. Strong; (2) States of Matter: Gerald R. Bakker and Laurence E. Strong; (3) Covalent Bond: Gerald R. Bakker and O. Theodor Benfey; (4) Ions: Wilmer J. Stratton; (5) Chemical Energy: Wilmer J. Stratton; (6) Resonance and Aromaticity: Gerald R. Bakker and O. Theodor Benfey; (7) Kinetics and Mechanisms: Gerald R. Bakker and O. Theodor Benfey; (8) Biochemistry: Gerald R. Bakker and Laurence E. Strong; (9) Thermodynamics: Laurence E. Strong; (10) Structure and Periodicity: Wilmer J. Stratton; (11) Seminar: Staff; (12) Independent Study: Staff.

## FUTURE CHANGES

A number of questions regarding the present form of the curriculum are currently receiving attention. Among them are: (a) Whether the two "streams" of students entering Chemistry 46, "Ions," have sufficiently similar training to permit satisfactory joint instruction; (b) Whether there is avoidable overlap between Chemistry 11, 12 and 46, and also between Chemistry 12, 50 and 54; (c) The proper place for introducing elementary quantum mechanics; and (d) How the laboratory program in all of the courses can be redesigned to achieve the goals set down.

An experimental curriculum tends to keep on changing. Changes in one course often require changes in others. Faculty members therefore find themselves quite often consulting each other, and are frequently stimulated to explore new ways of presenting materials as a result of such consultations. Students also get involved in useful discussions with faculty members regarding methods of presenting chemistry. The attached outlines of courses should, accordingly, be seen only as a progress report, presenting the current state of the Earlham curriculum. We have every intention of continuing to change and improve it.

## ACKNOWLEDGEMENTS

We are indebted to Reino Hakala (current address: University of Syracuse) who taught in the department and contributed many significant ideas at the beginning of our curriculum development; to Dr. Robert Pearson (current address: University of Ghana) for his considerable assistance during the years 1961-1963; and to Walter E. Hunter for help in the development and use of programmed instruction materials.

Extensive curricular innovations of the type described are impossible without institutional sympathy and support. Earlham College administrators have contributed both encouragement and funds. A grant from the Smith, Kline, and French Foundation made possible the hiring of an additional staff person for two years and the acquisition of equipment for new laboratory programs. Generous grants from E. I. DuPont de Nemours and Co. and from the Lubrizol Foundation have made possible the securing of further equipment appropriate to the new courses.

## COURSE CONTENT OUTLINES

### CHEMISTRY 11: PARTICLES OF CHEMISTRY (Fall Term—First Year)

Sessions: 30, 1-hour classes; 10, 3-hour laboratory periods; 8 quiz and discussion sessions.

Texts: Sienko and Plane (S & P);<sup>6</sup> (CBA);<sup>4</sup> and programmed material on electrostatic potential energy and charge cloud calculations.

Chemistry is introduced as the interpretation of changes observed when materials are mixed together. The properties of systems are studied as a function of the differences observed between the states of a system before and after the components are mixed. The investigation leads to operational definitions of simple mixtures, solutions, compounds, elements, and reactions. The stoichiometry of reactions in general, and compound formation in particular, develops fairly logically from observations. A major operational tool used is the method of continuous variation.

It is repeatedly emphasized that collection of observable data is one thing, but a perception that the data have meaning is quite another—something not achieved by mere logical analysis of the data. Meaning arises through the human introduction of imaginative ideas, i.e., postulates and deductions.

The problem of understanding systems of substances is developed through postulating that observed changes are the reflections of structural changes. It is assumed that there are structural units—atoms, molecules, and ions. Further investigation suggests that chemical reactions and materials generally have an electrical nature. Useful structures and their changes are then developed in terms of the assumption of electrons and nuclei.

To analyze, in an elementary way, the logical consequences of the assumption that electrons and nuclei are appropriate structural units, the charge cloud model developed by G. Kimball is introduced. Emphasis in this model is on the energy of systems of diffused negative charge and concentrated positive charge. Simple geometry appears in this way, based on the packing of spheres to form tetrahedra. A few calculations of energy and size are worked out. With a background of the postulational scheme using charge cloud ideas, a presentation is given of the hybridized atomic orbital theory. Comparison of the charge cloud model and the hybridized atomic orbital model provides opportunity to stress the proposition that theories are judged not by their "truth" but by their utility.

### *Lecture Outline*

- I. MIXTURES OF MATERIALS—3 hours (S & P  
Chap. 1 and 2; CBA Chap. 1 and 2).
  - A. Simple mixtures and solutions
  - B. Interaction operationally defined

- C. Characteristic properties
- D. Chemical reaction
- E. Systems and their states
- F. Operational and conceptual definitions

<sup>6</sup> SIENKO, M. J., AND PLANE, R. A., "Chemistry," McGraw-Hill Book Co., Inc., New York, 1961.

**II. NATURE OF A CHEMICAL REACTION—6 hours (CBA Chap. 3; S & P Chap. 5).**

- A. The search for simplicity
- B. Classification of materials
- C. Compounds and elements
- D. Reactions of gases
- E. Atoms and molecules as structural units
- F. Formulas and equations
- G. Chemical change as structural change
- H. Chemical change and energy transfer
  - 1. Heat
  - 2. Work
  - 3. Electricity
- I. Electric interaction in chemical systems

**III. NATURE OF SUBSTANCES—4 hours (CBA Chap. 4, 5, and 6; S & P Chap. 2 and 3).**

- A. Electric charge and its relation to matter
  - 1. Thermoelectricity
  - 2. Photoelectricity
  - 3. Cathode rays
  - 4. Positive ion beams
- B. Structural units of substances
  - 1. *Alpha* particle scattering
  - 2. The nuclear atom
  - 3. Electrons and nuclei
  - 4. Isotopes
  - 5. Mass and volume

**IV. ELECTRON-NUCLEUS INTERACTION — 5 hours (S & P Chap. 4; CBA Chap. 7).**

- A. Electrostatic potential energy
- B. Postulates for a model of matter
- C. Charge cloud models of some molecules
- D. Interpretation of chemical change
- E. Limitations of charge cloud model

**V. ANOTHER THEORY OF ATOMIC STRUCTURE—6 hours (CBA Chap. 10; S & P pp. 46-76).**

- A. Rutherford's nuclear atom
- B. Bohr's quantized atom
  - 1. The resolution of difficulties
  - 2. The theory
  - 3. The problems raised
- C. Phenomena to be explained
  - 1. Ionization
  - 2. Spectral emission
  - 3. Wave and particle postulates
- D. The answers of modern quantum mechanics
  - 1. Electron clouds
  - 2. Electron orbitals
  - 3. How electrons fill space
- E. The *Aufbau* principle
- F. Periodicity

**VI. CHEMICAL BONDING—6 hours (S & P Chap. 4).**

- A. Covalent bonds (CBA Chap. 7)
  - 1. Properties of molecules
  - 2. Hybrid bond modification
- B. Ionic bonds (CBA Chap. 12 and 13)
  - 1. Independence of ions
  - 2. Additivity of properties
- C. Metallic bonds (CBA Chap. 11)
- D. Electrostatic nature of chemical bonds
- E. Acid-base reactions interpreted by nuclear repulsion

*Laboratory*

Mimeographed materials, with library references in connection with Experiment 8, are used.

In the laboratory a study is carried out to elucidate the stoichiometry of several reactions. Volume changes, mass changes, temperature changes, and energy transfer are each applied to appropriate chemical systems. The methods of continuous variation and of titration are used extensively.

A major student assignment at the end of the course is the investigation of a chemical system. Each student is given one system from a large set of possibilities. In general, these systems consist of a pair of compounds in aqueous solutions which, when mixed, react to form a precipitate. The student is asked to use the techniques already developed in previous laboratory work to obtain sufficient data to form a judgment on the nature of the observed reaction. After several weeks of laboratory work and library study, a brief paper is prepared describing the work, proposing an interpretation, and showing how the data obtained support the proposed interpretation.

*Laboratory experiments*

1. The Black Box: a study of the interpretation of observations made on a loose object in a sealed box;
2.  $\text{PbI}_2$  Precipitation: continuous variation study of the reaction  $2\text{KI}(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{PbI}_2(\text{aq}) + 2\text{KNO}_3(\text{aq})$

→  $\text{PbI}_2$  (s) + 2  $\text{KNO}_3$  (aq); 3. Relative Reaction Masses: titration method used to compare quantitatively the reaction with  $\text{Pb}(\text{NO}_3)_2$  (aq) of  $\text{LiI}$ ,  $\text{NaI}$ ,  $\text{KI}$ ,  $\text{RbI}$ , and  $\text{CsI}$ ; 4. Heat and Chemical Change; 5. Calorimetric Titration: thermometric titration of  $\text{HCl}$  (aq) and  $\text{NaOH}$  (aq); 6. Geometry of Electron Pairs: a study of the packing of spheres and the significance of radius ratios (electron pairs are assumed to be capable of representation by equivalent spheres of uniform charge density); 7. Solutions: freezing point depression as a function of concentration for some acids and an alcohol are compared with chemical reactivity; 8. Investigation of an assigned system.

### **CHEMISTRY 12: STATES OF MATTER (Winter Term—First Year)**

Prerequisite: Chemistry 11 or examination.

Sessions: 30, 1-hour classes; 8, 1-hour quiz sessions; 10, 3-hour laboratory sessions.

Texts: Same as for Chemistry 11.

The major concept developed is that of the kinetic-molecular theory of matter. This development proceeds by a consideration of energy transfer for reactions conducted isothermally. The idea of enthalpy is introduced. Initial consideration of phase changes points up the inability of the electron-nuclear models to account for these changes. The postulates of the kinetic-molecular theory are first introduced to deal with properties of gases, and then extended to liquids and solids. Equilibrium among phases is discussed briefly. Much of the descriptive material is drawn from the properties of the elements, and emphasis is placed on periodic relationships.

A major student assignment is a library research paper on an element, with each student assigned a different element. The papers are expected to show how some of the properties of an element can be interrelated through ideas about structure and energy.

#### *Lecture Outline*

- I. ENERGY—6 hours (CBA Chap. 9).
  - A. Heat transfer, chemical reaction, and enthalpy change
  - B. Enthalpy diagrams and Hess' law
  - C. Enthalpy and structure
  - D. Direction of change
- II. KINETIC-MOLECULAR THEORY—10 hours (CBA Chap. 8, 11, 12; S & P Chap. 6-9).
  - A. Gases
    - 1. Experimental properties of gases
    - 2. Derivation of ideal gas law
    - 3. Real gases, electron-nucleus models
  - B. Liquids
    - 1. Properties and structure
    - 2. Gas-liquid equilibrium
  - C. Solids
    - 1. Packing of spheres
    - 2. Crystals, electrons, and nuclei
    - 3. Solid-liquid equilibrium
- D. Solutions
  - 1. Homogeneity—random arrangement
  - 2. Interaction—structure
  - 3. Raoult's law
- III. PERIODICITY—8 hours (S & P Part II).
  - A. Family relationships among elements
    - 1. Uniformity and trends
    - 2. Property-structure relationships
  - B. Period relationships among elements
    - 1. Relation between properties and number of electrons per nucleus
  - C. Prediction of bond types
    - 1. Enthalpy—electronegativity considerations
    - 2. Charge-size relationships
- IV. ISOELECTRONIC GROUPINGS—6 hours.
  - A. Properties of hydrides of representative elements
  - B. Acid-base characteristics

#### *Laboratory Experiments (carried out in 1963-64)*

- 1. Pressure-Volume Properties of Gases: syringes, and capillary tubes containing a mercury slug are used to study P-V relations for several gases; 2. Velocity of Gas Motion: measurement of travel time down a glass tube for  $\text{HCl-NH}_3$ , and several volatile amines; 3. Acid-Base Titration: starting with standard  $\text{NaOH}$ , a standardized solution of  $\text{NH}_3$  (aq) is prepared; 4. Enthalpy of Formation of  $\text{NH}_4\text{Cl}$  (s): enthalpy change is measured for  $\text{NH}_3$  (aq) +  $\text{HCl}$  (aq) and for  $\text{NH}_4\text{Cl}$  (s) →  $\text{NH}_4\text{Cl}$  (aq)—from these data and the literature a calculation is made to give  $\Delta H_f$  for  $\text{NH}_4\text{Cl}$  (s); 5. Reaction Sto-

chiometry and Gas Evolution: continuous variation study of  $\text{CO}_2$  volume for the reaction of  $\text{NaHCO}_3$  (aq) and  $\text{HCl}$  (aq); 6. Heat of Vaporization of a Liquid: distillation of water is carried out to give  $\Delta H_v$ ; 7. Phase Diagram for Biphenyl-Naphthalene System; 8. Properties of Halogens: descriptive chemistry of the halogens is explored through a series of questions posed for the student in the laboratory.

### **CHEMISTRY 13: COVALENT BOND (Spring Term—First Year)**

Prerequisite: "States of Matter."

Sessions: 30, 1-hour classes; 8 quiz and discussion sessions; 10, 3-hour laboratory sessions.

Reading Materials: Text, Morrison and Boyd (M);<sup>7</sup> CBA;<sup>8</sup> Benfey (B);<sup>9</sup> Kieffer (S);<sup>9</sup> and programmed materials on the nomenclature of organic compounds (mimeographed).

This course focuses initially on a single, idealized bond type, the nonpolar covalent bond, and then deals with nonpolar and polar covalent compounds of the elements found in the northeast corner of the periodic table. Emphasis is placed on the chemistry of aliphatic carbon compounds. Acid-base relationships and stereochemistry are developed. Relations between the molecules in the isoelectronic set  $\text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$  and between their alkyl derivatives are stressed.

Each student is expected to write a term paper on the preparation, physical properties, and chemical properties of a complex covalent compound. The properties of the compound are to be related to its structural and energy characteristics.

#### *Lecture Outline*

**INTRODUCTION:** The evolution of the universe and the evolution of man's thought about the universe  
—1 hour.<sup>10</sup>

- I. MOLECULES—1 hour (CBA pp. 76 ff.; and mimeographed material).
  - A. Dalton, Avogadro, Gay-Lussac, and Berzelius on the atomicity of gas molecules
- II. THE COVALENT BOND—2 hours.
  - A. The synthesis of an organic compound—urea (B Chap. 3)
  - B. The discovery of radicals (B Chap. 4)
  - C. Substitution reactions not explainable electrochemically (B Chap. 5)
  - D. Valence, tetravalence of carbon and chain-forming capacity of carbon atoms (B Chap. 7-9)
- III. THE COVALENT BOND: The Current View—1 hour (M Chap. 1).
  - A. The hydrogen molecule; orbitals, the direction of bonds (S p. 98); hybridization
- IV. NONPOLAR COVALENT BOND: Saturated Hydrocarbons, Alkanes—3 hours (M Chap. 2 and 3).
  - A. Homologous series
  - B. Physical properties of alkanes, relation to structure
  - C. Methods of preparation
  - D. Reactions of alkanes
    - 1. The chlorination of methane
  - E. Isomerism
- V. POLAR COVALENT BONDS (CBA pp. 522 ff.).
  - A. Compounds of carbon with Group VII elements: alkyl halides—5 hours (M Chap. 2, 3, & 13)
    - 1. Preparation
    - 2. Physical properties: relation to structure
    - 3. Chemical reactions
      - a. The displacement reaction
    - 4. Effects of structure on reactivity
    - 5. Stereochemistry (M Sect. 11-15 to 11-24)

<sup>7</sup> MORRISON, R. T., AND BOYD, R. N., "Organic Chemistry," Allyn and Bacon, Inc., Boston, 1959.

<sup>8</sup> BENFEY, O. T., "From Vital Force to Structural Formulas," Houghton Mifflin Co., Boston, 1964.

<sup>9</sup> KIEFFER, W. F., Ed., "Supplementary Readings for Chemical Bond Approach," Chemical Education Publishing Co., Easton, Pa., 1961.

<sup>10</sup> GAMOW, G., "The Creation of the Universe," The Viking Press, New York, Compass Books Edition, 1956.

- B. Carbon compounds containing Group VI elements—3 hours**
  - 1. Alcohols (M Chap. 11 and 12; CBA pp. 739 ff.); comparison with water
    - a. Hydrogen bonding (S pp. 172 and 179)
  - 2. Ethers (M Chap. 15)
  - 3. Mercaptans (thioalcohols) and thioethers (cf. Noller,<sup>11</sup> Karrer,<sup>12</sup> or Fieser);<sup>13</sup> H<sub>2</sub>S vs. H<sub>2</sub>O
  - 4. Polyfunctional compounds
    - a. Ethylene glycol and glycerol (M Chap. 24)
    - b. Effect of several functional groups on physical and chemical properties
  - 5. The hydroxyl group in other compounds
  - 6. The nature of a functional group
- C. Ammonia and its alkyl derivatives: amines—3 hours (M Chap. 19 and 20)**
  - 1. Sources
  - 2. Basic character of ammonia and amines (cf. CBA Chap. 16)
    - a. Ionization constant of bases
    - b. Effect of structure on base strength
    - c. Stereochemistry of nitrogen
  - 3. Methods of preparation
  - 4. Chemical reactions
  - 5. Differentiation between primary, secondary and tertiary amines

#### **VI. MULTIPLE BONDS.**

- A. Nonpolar double bonds—4 hours (M Chap. 4 and 5)**
  - 1. Ethylene
  - 2. The shape of the double bond
    - a. *Pi* bonds, *sigma* bonds, and "banana" bonds (S pp. 196 and 202)
    - b. Restricted rotation and *cis-trans* isomerism
  - 3. Alkenes
    - a. Methods of preparation
    - b. Chemical properties
      - (1) Addition reactions
      - (2) Polymerization: plastics (M pp. 184 and 188-191), giant molecules (S p. 192)
    - c. Butadiene, isoprene, natural and artificial rubber (M pp. 175-192)
- B. Polar double bonds: the carbonyl group—2 hours (M Chap. 23)**
  - 1. Electrical nature of carbonyl group
  - 2. Aldehydes and ketones
    - a. Methods of preparation—oxidation
    - b. Addition to the carbonyl group
    - c. Grignard reactions
    - d. Addition with elimination of water
    - e. Condensations
    - f. Differentiation between aldehydes and ketones
- C. The triple bond—1 hour**
  - 1. Nonpolar: acetylene, alkynes (M Chap. 6; S p. 202)
  - 2. Polar: nitriles (M pp. 441-4, 527-9)

#### **VII. COMPLEX FUNCTIONAL GROUPS—obtained by combining two simple functional groups—2 hours.**

- A. Carbonyl and hydroxyl: carboxylic acids (M Chap. 16)**
  - 1. Proof of structure
  - 2. Acid character, resonance, ionization constants (CBA Chap. 16)
  - 3. Physical properties and hydrogen-bonding
  - 4. Preparation and reactions
  - 5. Salts of carboxylic acids; soaps (M pp. 493-6)

<sup>11</sup> NOLLER, C. R., "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, 1957.

<sup>12</sup> KARRER, P., "Organic Chemistry," American Elsevier Publishing Co., Inc., New York, 1950.

<sup>13</sup> FIESER, L. F., AND FIESER, M., "Organic Chemistry," 3rd ed., Reinhold Publishing Corp., New York, 1956.

B. Carbonyl and alkoxy: esters (M pp. 482-499)

1. Occurrence: fats
2. Esterification and saponification
3. Equilibrium constant—review

C. Carbonyl and amino: amides and proteins (M pp. 481-482 and 866-883)

D. Acid halides and anhydrides (M pp. 473-480)

**VIII. INTERACTION OF FUNCTIONAL GROUPS—2 hours.**

A. Halogen acids (M pp. 446 and 461-2)

1. Principles of ring formation and ring stability: cycloalkanes (M Chap. 7)

B. Amino acids (M pp. 858-866)

C. Hydroxy acids (M Chap. 27)

*Laboratory* (Chemistry 13)

The laboratory introduces several new experimental techniques, syntheses of a number of carbon compounds, the study of the effect of variables on yield, and the characterization and identification of functional groups.

*Experiments* (mimeographed instructions throughout):

1. Melting point determinations, purification by recrystallization to constant melting point, identification of unknowns by mixture melting point determination, transition temperature of mercuric iodide (2 sessions); 2. The preparation of *n*-butyl bromide and *tert*-butyl chloride, carried out as a class project with different students using different reflux times, concentrations, and alkyl halides (1½ sessions); 3. Use of molecular models (wax and stick) for organic stereochemistry and isomer determination (½ session); 4. Williamson ether synthesis of alkyl phenyl ethers (1 session); 5. Synthesis of a crystalline covalent solid: idoform (1 session); 6. Preparation of esters, conductance tests on reagents and products (1½ sessions); 7. Comparative tests on alkanes and alkenes (½ session); 8. Identification of functional groups: ROH, R(OH)<sub>x</sub>, RNH<sub>2</sub>, R(NH<sub>2</sub>)<sub>x</sub>, RCO<sub>2</sub>H, R(CO<sub>2</sub>H)<sub>x</sub>, RH, R<sub>2</sub>C=CR<sub>2</sub>, RCl, RBr, RI, RCO<sub>2</sub>M (2 sessions).

**CHEMISTRY 46: IONS (Winter Term—Second Year)**

Prerequisite: "Covalent Bond."

Sessions: 28, 1-hour classes; 18, 3-hour laboratory periods.

Texts (1964): King,<sup>14</sup> first half only; Skoog and West (S & W),<sup>15</sup> selected chapters.

The course is designed to give students a thorough acquaintance with the chemistry of ionic compounds. The emphasis is almost entirely on aqueous solutions, since the chemistry of solutions includes a number of important topics, and since the nature of ionic crystals is dealt with in some detail in the first-year courses. Parallel to the discussion of ionic solutions, a second emphasis in the course is the development of principles and techniques of quantitative analysis.

*Lecture*

The lectures and reading assignments are organized around the following four major topics:

- (1) **IONIC REACTIONS IN AQUEOUS SOLUTION.** (See outline below.)
- (2) **THEORY OF IONIC SOLUTIONS.** A study of colligative properties, conductivity data, and ionic strength effects leads to introduction of the modern theory of ionic solutions. Activity coefficients, ionic strength, and the Debye-Hückel equation are used extensively, and these are tied to several laboratory studies. Emphasis is placed on ionic solutions as dramatic examples of "nonideal" behavior, and on the problems involved in developing an adequate theory.

<sup>14</sup> KING, E. J., "Qualitative Analysis and Electrolytic Solutions," Harcourt, Brace and Co., New York, 1959.

<sup>15</sup> SKOOG, D. A., AND WEST, D. M., "Fundamentals of Analytical Chemistry," Holt, Rinehart and Winston, Inc., New York, 1963.

(3) IONIC EQUILIBRIUM. This is the largest single topic in the course. The equilibrium concept is developed using experimental data, with emphasis on ionization, solubility, and solvent distribution equilibria. Thermodynamic equilibrium constants and ionic strength effects are included throughout. Several case studies of equilibrium systems are explored in detail. An introduction to principles of qualitative analysis is included, with emphasis on the application of ionic equilibria.

(4) PRINCIPLES OF QUANTITATIVE ANALYSIS. Approximately one lecture per week is devoted to the principles and techniques of classical volumetric, gravimetric, and colorimetric methods. The study of analytical principles ties in rather closely with the study of ionic equilibrium. An effort is made to present the "big picture" of analysis, with emphasis on general principles, major types of analyses, and evaluation of different analytical procedures. One goal of the work in analytical chemistry (both lecture and laboratory) is to take students up to the point where they can use the literature to locate possible methods of analysis for a given substance, are able to evaluate the relative advantages and disadvantages of the various methods, and can successfully carry out the analysis.

#### *Lecture Outline*

- I. WATER—1 hour (King Chap. 1).
  - A. Nature and properties of pure water
  - B. Relation of water to other solvents
  - C. Effect of ionic substances on the properties of water and vice versa
- II. CONCENTRATIONS OF SOLUTIONS—1 hour (King Chap. 2).
  - A. Definitions and usefulness of various units
  - B. Application to calculations of volumetric analysis
- III. IONIC REACTIONS AND EQUATIONS—3 hours.
  - A. Why ionic reactions occur in aqueous solution
  - B. The writing of equations for ionic reactions (programmed instruction unit, mimeographed)
  - C. Oxidation-reduction reactions and equations (programmed instruction unit, mimeographed)
  - D. Survey of important oxidation states by families within the periodic table
  - E. Nomenclature of inorganic compounds
- IV. PROPERTIES OF IONIC SOLUTIONS—5 hours (King Chap. 2 and 5).
  - A. Colligative properties of ideal solutions (programmed instruction unit, mimeographed)
  - B. Evidence for the existence of ions
  - C. Colligative properties of ionic solutions
  - D. Electrolytic conductivity, equivalent conductance and concentration
  - E. Theories of ionization; strong and weak electrolytes
  - F. Ionic strength and activity concepts; Debye-Hückel theory (mimeographed supplement)
- V. COORDINATION COMPOUNDS—1 hour (King Chap. 6).
  - A. Types of ligands; chelating agents
  - B. Geometries of complexes with various metals and ligands
  - C. Nomenclature
- VI. IONIC EQUILIBRIUM—4 hours (King Chap. 7-9).
  - A. Law of chemical equilibrium; equilibrium constants
  - B. Ionization equilibria
  - C. Common ion effect
  - D. Distribution equilibria
  - E. Solubility equilibria
- VII. APPLICATIONS OF EQUILIBRIUM CONCEPTS—5 hours (King portions of Chap. 10-14).
  - A. pH
  - B. Brønsted acid-base equilibria
  - C. Buffer solutions

- D. Indicator equilibria
- E. Complex-ion equilibria
- F. Competing equilibria
- G. Qualitative analysis
  - 1. Problems of separation and identification
  - 2. Study of Groups I and III of the hydrogen sulfide scheme
  - 3. Equilibrium calculations
- H. Distribution of acetic acid between water and ether: evidence for dimerization
- I. Ionization of methyl red<sup>16</sup>

**VIII. PRINCIPLES AND TECHNIQUES OF QUANTITATIVE ANALYSIS—8 to 10 hours.**

- A. Introduction to precision volumetric analysis (S & W Chap. 1, 2, 3, 10, and 11)
  - 1. Techniques
  - 2. Neutralization titrations
  - 3. Calculations
  - 4. Treatment of errors
  - 5. Complex-formation titrations
- B. The analytical balance (including single pan type)
- C. Spectrophotometry (S & W Chap. 28)
  - 1. Types of spectrophotometry (ultraviolet, visible, infrared)
  - 2. Beer's law
  - 3. Instrumentation
  - 4. Applications
- D. Survey of methods for chloride analysis (S & W Chap. 12)
- E. Oxidation-reduction titrations (portions of S & W Chap. 17-22)
  - 1. Equivalent weight and normality (programmed instruction unit, mimeographed)
  - 2. Common redox methods
- F. Some additional aspects of analysis
  - 1. End point errors
  - 2. Equilibrium calculations
  - 3. Primary standards
- G. Gravimetric methods (portions of S & W Chap. 4-8)
  - 1. Techniques
  - 2. Mechanism of precipitate formation
  - 3. Homogeneous precipitation methods

*Laboratory Program*

The laboratory work has several objectives, including: (1) to provide experience with the preparation, isolation, and analysis of pure ionic compounds; (2) to develop skill in high-precision analysis; (3) to give first-hand experience with representative methods of volumetric, gravimetric, and colorimetric analysis; and (4) to conduct studies of several equilibrium systems, using methods of quantitative analysis. A considerable number of experiments have been tried out over the past five years, but only a portion of them are used in any one year. Changes are made from year to year, not so much because of improved experiments, but in order to provide variety, and to maintain student interest at a high level. An effort is made to include at least one really *new* experiment each year. This not only provides stimulation and satisfaction for the instructor, but it also gives the students a sense of participation in a creative venture. There appears to be no end of possibilities for interesting and significant experiments!

The particular experiments used during 1963-64 were as follows:

1. Neutralization titration exercise, HCl *vs.* NaOH, NaOH *vs.* sulfamic acid, emphasis on high-precision results (mimeographed) (2 sessions); 2. Preparation of crystalline copper(II) sulfate from copper (mimeographed); 3. Determination of the solubility of calcium sulfate as a function of con-

<sup>16</sup> RAMETTE, R. W., *J. Phys. Chem.*, 66, 527 (1962).

centration of added electrolytes, complex-formation titration using EDTA (different electrolytes used from year to year) (mimeographed, adapted from Ramette);<sup>17</sup> 4. Colorimetry, Beer's law graph for iron, using 1,10-phenanthroline, and utilizing this method for the determination of the solubility product of iron(II) oxalate (mimeographed); 5. Research study of a new compound,  $\text{FeCl}_2(\text{CH}_3\text{OH})_x$ : (a) preparation under an inert atmosphere, (b) complete analysis, using colorimetric, volumetric, and gravimetric methods (mimeographed) (3 sessions); 6. Gravimetric determination of lead as chromate, using both homogeneous and heterogeneous methods (mimeographed); 7. Determination of the activity coefficient of silver bromate in sodium perchlorate solutions: iodometric titration with thiosulfate—each student works at a different ionic strength and the results are assembled graphically to test the validity of the Debye-Hückel equation (mimeographed, adapted from R. W. Ramette, private communication) (2 sessions); 8. Determination of copper(II) iodate solubility as a function of acidity, graphical calculation of  $K_{sp}$  for copper iodate and  $K_a$  for iodic acid (mimeographed, taken from Ramette)<sup>18</sup> (2 sessions); 9. The dissociation constant for  $\text{Fe}(\text{CNS})^{++}$ , spectrophotometric laboratory demonstration (mimeographed, taken from Ramette);<sup>19</sup> 10. Analysis of two unknown samples: magnesium by EDTA and oxalate by permanganate (S & W).

Experiments number 3, 7, 8, and 9 are examples of experiments that can be made more interesting by including modifications from year to year of such variables as temperature, ionic strength, and nature of the added electrolytes.

#### **CHEMISTRY 50: CHEMICAL ENERGY (Spring Term—Second Year)**

Prerequisites: "Ions"; freshman mathematics (college physics is recommended).

Sessions: 28, 1-hour classes; 18, 3-hour laboratory periods.

Text: Strong and Stratton;<sup>20</sup> supplementary texts: Barrow;<sup>21</sup> Latimer;<sup>22</sup> Skoog and West (S & W).<sup>15</sup>

The major objective of this course is to present an introduction to the fundamentals of chemical thermodynamics in such a way as to help the student see the significance of the subject in the study of chemical reactions. An effort is made to develop the basic concepts from experimental data and to show the logic of the interrelationships between the thermodynamic functions. The major emphasis is then placed on the application of these principles to the investigation of a wide variety of chemical systems. Entropy receives considerably more emphasis than in most elementary discussions of chemical thermodynamics. Extensive problem assignments are given, for which students are sent to the standard thermodynamic reference tables, and in some cases to the original literature, in order to obtain the necessary data. The presentation uses relatively little calculus, with much of the rigorous mathematical development postponed to the thermodynamics course in the senior year. Some of the usual thermodynamic topics which are not covered in any detail in this course are heat capacities of gases, the Carnot cycle, the Gibbs-Helmholtz equation, phase equilibria, and statistical thermodynamics (cf. Chemistry 54).

#### *Lecture Outline<sup>23</sup>*

##### **I. FUNDAMENTAL ENERGY CONCEPTS—1 hour.**

- A. History
- B. Different forms of energy and their interconnections
- C. The conservation principle
- D. Energy units

##### **II. AN OVERVIEW OF CHEMICAL THERMODYNAMICS—3 hours.**

- A. The central question: What factors determine the feasibility of chemical change?
  - 1. Data on heats of reaction
  - 2. Data on electrode potentials

<sup>17</sup> RAMETTE, R. W., *J. Chem. Educ.*, 33, 610 (1956).

<sup>18</sup> RAMETTE, R. W., *J. Chem. Educ.*, 33, 191 (1959).

<sup>19</sup> RAMETTE, R. W., *J. Chem. Educ.*, 40, 71 (1963).

<sup>20</sup> STRONG, L. E., AND STRATTON, W. J., "Chemical Energy," Reinhold Publishing Corp., New York, (in press).

<sup>21</sup> BARROW, G. M., "Physical Chemistry," McGraw-Hill Book Co., New York, 1961.

<sup>22</sup> LATIMER, W. M., "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, 1952.

<sup>23</sup> Except where otherwise noted the outline follows approximately the development in Strong and Stratton.<sup>20</sup>

- B. Introduction to three major experimental techniques (preparation for laboratory work)
  - 1. Calorimetric measurements
  - 2. Electric potential measurements
  - 3. Concentration measurements in equilibrium systems

**III. ENERGY AND ENTHALPY—2 hours.**

- A. Adiabatic processes; temperature-changing capacity
- B. Isothermal processes; heat transfer
- C. Constant pressure processes; enthalpy change ( $\Delta H$ )
- D. Constant volume processes; internal energy change ( $\Delta E$ )
- E. Relation between  $\Delta E$  and  $\Delta H$
- F. First law of thermodynamics

**IV. THE ARITHMETIC OF THERMOCHEMICAL CHANGE—3 hours.**

- A. Specification of change; change *vs.* process
- B. Indirect determination of energy change; Hess' law
- C. Use of energy level diagrams
- D. Enthalpy of formation
- E. Enthalpy of combustion
- F. Enthalpy changes involving ions in aqueous solution
- G. Use of standard thermodynamic reference tables
- H. Temperature effect on  $\Delta H$

**V. APPLICATIONS OF ENTHALPY CHANGE TO STUDIES OF STRUCTURE—3 hours**

- A. Analysis of formation enthalpies for the alkali-metal halides
  - 1. Born-Haber cycle
  - 2. Interpretation of the trends within the series
- B. Solubility of ionic crystals; lattice enthalpies and hydration enthalpies
- C. Covalent bond formation energies
  - 1. Resonance effects
  - 2. Steric effects
  - 3. Crystal field stabilization

**VI. SPONTANEOUS PROCESSES—4 hours.**

- A. Principle of minimum potential energy
- B. The anomaly of endothermic reactions
- C. Statistical aspects of change
- D. Reversible and irreversible processes
- E. Entropy and the second law of thermodynamics
- F. Free energy and maximum work
- G. Electric energy; electrochemical cells
- H. Concentration difference and free energy change
  - I. Electric potentials and the Nernst equation

**VII. EQUILIBRIUM—2 hours.**

- A. Relation between free energy, entropy, and equilibrium
- B. The acetic acid-water system
- C. The reaction between iron(III) and silver

**VIII. ABSOLUTE ENTROPY—2 hours.**

- A. Heat capacities and entropy change
- B. Third law of thermodynamics
- C. Correlation of entropy with structure

**IX. THERMODYNAMIC STUDY OF SELECTED CHEMICAL SYSTEMS—4 hours.**

- A. Constant enthalpy processes
  - 1. Mixing of ideal gases
  - 2. Electrochemical concentration cells
- B. Phase changes
- C. Formation reactions of some isoelectric series of gaseous compounds

- D. Alkali-metal halide formation
- E. Solubility of ionic crystals
- F. Ionic reactions in aqueous solution: neutralization and precipitation
- G. Effect of temperature on reaction feasibility; comparison of energy and entropy contributions at different temperatures
- H. Entropy and free energy of covalent bond formation

X. USE OF OXIDATION POTENTIALS—1 hour (Latimer selected reading).

XI. ELECTRICAL MEASUREMENTS—3 hours (S & W Chap. 22, 24, and 25).

- A. Electrical circuits and measuring devices
- B. The potentiometer principle
- C. Applications of the Nernst equation
  - 1. Potentiometric titrations
  - 2. Determination of  $E^\circ$
  - 3. Determination of activity coefficients

*Laboratory Program (Chemistry 50)*

The laboratory work has two major objectives: (1) application of thermodynamic principles to the study of selected chemical systems, and (2) introduction of a variety of instrumental techniques. Potentiometric methods are emphasized since these are tied rather closely to thermodynamic principles, but conductometric and spectrophotometric methods are also introduced. The program during 1963-64 was approximately as follows. (Assignments were made individually to the students working in pairs; however, most students did experiments 1-5.)

1. Qualitative analysis (Three laboratory periods at the beginning of the term are devoted to an introduction to systematic cation analysis; this has no connection with the course, but relates to lecture material in Chemistry 46 at the end of the previous term.) (mimeographed); 2. Calorimetry: a careful study of one or two ionic reactions (2 periods) (mimeographed); 3. Potentiometric study of an electrochemical cell as a function of temperature: calculation of free energy, entropy and enthalpy changes (2 periods) (cf. Daniels, *et al.*);<sup>24</sup> 4. Spectrophotometric determination of  $pK_a$  for an indicator (2 periods) (cf. Reilley and Sawyer);<sup>25</sup> 5. Instrumental titrations (4 periods): pH (S & W p. 572), redox and precipitation (S & W pp. 572-3), conductometric (S & W p. 584), photometric (Reilley and Sawyer p. 147); 6. Comparison of the equilibrium constant and the electric potential for calculation of free energy change (cf. Daniels p. 202); 7. Measurement of electrochemical cell potential as a function of concentration: calculation of  $E^\circ$  and activity coefficients; 8. Construction of a simple potentiometric recorder and its utilization in potentiometric titrations (cf. Tabbutt);<sup>26</sup> 9. Studies of the solubility of lead iodide by means of direct potentiometry, several different potentiometric titrations, conductivity, and spectrophotometry (cf. Meites and Thomas).<sup>27</sup>

**CHEMISTRY 51: RESONANCE AND AROMATICITY (Fall Term—Third Year)**

Prerequisites: "Covalent Bond" ("Ions" and "Energy" are recommended).

Sessions: 30, 1-hour classes; 10, 4-5 hour laboratory sessions.

Text: Morrison and Boyd.<sup>28</sup> Supplementary texts: Cartmell and Fowles;<sup>29</sup> Fuson;<sup>30</sup> Gilreath;<sup>31</sup> Gould;<sup>32</sup> Hine;<sup>33</sup> Streitwieser;<sup>34</sup> CBA;<sup>4</sup> Wheland.<sup>35</sup>

<sup>24</sup> DANIELS, F., *et al.*, "Experimental Physical Chemistry," 6th ed., McGraw-Hill Book Co., Inc., New York, 1962, p. 208.

<sup>25</sup> REILLE, C. N., AND SAWYER, D. T., "Experiments for Instrumental Methods," McGraw-Hill Book Co., Inc., New York, 1961, p. 153.

<sup>26</sup> TABBUTT, F., *J. Chem. Educ.*, 39, 611 (1962).

<sup>27</sup> MEITES, L., AND THOMAS, H. C., "Advanced Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, 1958, pp. 415-44.

<sup>28</sup> MORRISON, R. T., AND BOYD, R. N., "Organic Chemistry," Allyn and Bacon, Inc., Boston, 1959.

<sup>29</sup> CARTMELL, E., AND FOWLES, G.W.A., "Valency and Molecular Structure," 2nd ed., Butterworth & Co., Ltd., London, 1961.

<sup>30</sup> FUSON, R. C., "Reactions of Organic Compounds," John Wiley & Sons, Inc., New York, 1962.

<sup>31</sup> GILREATH, E. S., "Fundamental Concepts of Inorganic Chemistry," McGraw-Hill Book Co., Inc., New York, 1958.

<sup>32</sup> GOULD, E. S., "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, 1959.

<sup>33</sup> HINE, J., "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1956.

<sup>34</sup> STREITWIESER, A., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, 1961.

<sup>35</sup> WHELAND, G. W., "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, 1955.

The major concept of the course is that of polycentric bonding. An understanding of this concept is developed, and then used in the discussion of aromatic compounds and other conjugated systems. The laboratory work involves the preparation and analysis of aromatic compounds, and a study of the procedures used in their preparation.

After a brief review of bonding types, a number of examples are given to demonstrate that the concept of bicentric bonding is inadequate to explain large segments of chemistry. In order to understand both bi- and poly-centric bonding, an extensive, though qualitative, discussion of the valence bond and molecular orbital theories of bonding is introduced. The Schrödinger equation is discussed, and also the various forms of the amplitude function of the electron. Then bonding in molecules, ranging from the hydrogen molecule ion to benzene, is presented in valence bond and molecular orbital terms. The next step is the discussion of the types of reactions benzene undergoes, and how these are explained in terms of resonance theory. The idea of aromatic character is applied to a wide variety of nonbenzenoid compounds of unusual properties, and the use of the Hückel rule is discussed. Polynuclear aromatic compounds are also reviewed.

The reactions of benzene and substituted benzenes are handled in terms of electrophilic and nucleophilic substitution mechanisms. Some time is also devoted to the review of functional group reactions, discussion of diazonium salt reactions, and other reactions peculiar to aromatic compounds.

The effect of polycentric bonding in noncyclic systems is discussed, and variations in physical properties and chemical reactions are explained in the same manner as in the case of aromatic systems.

A six to seven page term paper is required, in which the student presents a carefully thought-out and documented case for or against the proposal that a particular substance, chosen by the student, has aromatic character. Evidence must, in all cases, be from the original literature except where the library does not have the journals.

#### Lecture Outline

- I. INTRODUCTION—1 hour (Noller;<sup>36</sup> Gilreath Chap. 4; CBA Chap. 7 and 10-12; Morrison Chap. 1-7, 11-13, 16, 19, 20, and 23—review).
  - A. Covalent, ionic, and metallic bonds
  - B. Charge cloud and atomic orbital theories
- II. FAILURE OF LOCALIZED BONDS—2 hours.
  - A. Chemical and physical properties unexplainable using localized bonds
  - B. The dramatic insight of Kekulé
- III. MODERN INTERPRETATION—5 hours (Cartmell Chap. 1-9; Maybury;<sup>37</sup> Pauling<sup>38</sup> Chap. 1, 4).
  - A. Qualitative derivation of the wave equation
  - B. The significance of  $\Psi, \Psi^2, 4\pi r^2 \Psi^2$
  - C. Valence bond theory (V.B.) and applications
  - D. Molecular orbital theory (M.O.) and applications
  - E. Comparison of V.B. and M.O. theories
  - F. Polyatomic molecules and the V.B. and M.O. theories
- IV. BENZENE—4 hours (Wheland Chap. 2 and pp. 75-105; Levine and Cole;<sup>39</sup> Morrison Chap. 8; Kursanov, *et al.*;<sup>40</sup> Tatevskie and Shakhparanov;<sup>41</sup> Hine pp. 1-34).
  - A. V. B. explanation of benzene
  - B. M. O. explanation of benzene
  - C. The "unusual" properties of benzene
  - D. Nitration of benzene
  - E. Resonance energy of benzene from heats of combustion
  - F. Russian misinterpretation of V. B. ideas
  - G. Rules for writing resonance forms

<sup>36</sup> NOLLER, C. R., *J. Chem. Educ.*, 27, 504 (1950).

<sup>37</sup> MAYBURY, R. M., *J. Chem. Educ.*, 39, 367 (1962).

<sup>38</sup> PAULING, L., "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, 1960.

<sup>39</sup> LEVINE, A. A., AND COLE, A. G., *J. Am. Chem. Soc.*, 54, 338 (1932).

<sup>40</sup> KURSANOV, D. N., *et al.*, *J. Chem. Educ.*, 29, 2 (1952).

<sup>41</sup> TATEVSKIE, V. M., AND SHAKHPARANOV, M. I., *J. Chem. Educ.*, 29, 13 (1952).

**V. AROMATIC COMPOUNDS AND THEIR PROPERTIES**—3 hours (Streitwieser pp. 237-247, 256-263; Coulson and Golebiewski;<sup>42</sup> Wheland and Mann;<sup>43</sup> Doering and Knox;<sup>44</sup> Collman *et al.*;<sup>45</sup> Sondheimer and Gaoni;<sup>46</sup> Breslow and Yuan;<sup>47</sup> West and Powell;<sup>48</sup> Morrison Chap. 31).

- A. Carbocyclic ring compounds
- B. Heterocyclic ring compounds
- C. Sandwich compounds
- D. Inorganic compounds such as phosphonitrilics and boron nitride
- E. Miscellaneous compounds such as sydnone, porphyrins, and metal chelates
- F. The derivation of Hückel's rule and current applications
- G. Polynuclear aromatics

**VI. ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS**—6 hours (Gould Chap. 11; Morrison Chap. 9, 10, and 14; Fuson Chap. 2 and 4-6; Brown and Nelson;<sup>49</sup> Woodward, *et al.*).<sup>50</sup>

- A. Orientation and activation-deactivation
- B. Nitration
- C. Friedel-Crafts alkylation: kinetic versus thermodynamic control
- D. Friedel-Crafts acylation: reactions of carbonyl compounds
- E. Halogenation

**VII. NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS**—1 hour.

- A. Orientation and activation-deactivation
- B. The benzyne intermediate

**VIII. AMINES**—2 hours (Morrison Chap. 21).

- A. Preparation and reactions
- B. Diazonium compounds

**IX. PHENOLS: Preparation and Reactions**—1 hour (Morrison Chap. 22).

**X. MULTIPLE DOUBLE BONDS**—5 hours (Goud pp. 85-88; Morrison Chap. 26 and 28).

- A. Allenes
- B. Conjugated double bonds
  - 1. Free radical and ionic addition reactions
  - 2. Diels-Alder reaction
- C. Color in conjugated systems
  - 1. M.O. and V.B. explanations
  - 2. Light absorption in long conjugated systems
  - 3. Behavior of methyl orange
- D. Conjugate addition
  - 1. Reaction of alcohols with carbonyl compounds and conjugated carbonyl compounds
  - 2. Reaction of amines with carbonyl compounds and conjugated carbonyl compounds
  - 3. Reaction of enolates with carbonyl compounds and conjugated carbonyl compounds

#### *Laboratory Program (Chemistry 51)*

The laboratory program is intended to be kept from being an exercise in following recipes. Students are sometimes given directions to follow; at other times they have to find the best procedure for a reaction; and at still other times they are asked to devise a procedure on their own. The students are encouraged to compare results when different procedures are used. Another innovation in this course is the emphasis on product purification and quantitative organic analysis.

<sup>42</sup> COULSON, C. A., AND GOLEBIOWSKI, A., *Tetrahedron*, 11, 125 (1960).

<sup>43</sup> WHELAND, G. W., AND MANN, D. E., *J. Chem. Phys.*, 17, 284 (1949).

<sup>44</sup> DOERING, W. von E., AND KNOX, L. H., *J. Am. Chem. Soc.*, 76, 3203 (1954).

<sup>45</sup> COLLMAN, J. P., *et al.*, *J. Am. Chem. Soc.*, 83, 531 (1961).

<sup>46</sup> SONDEIMER, F., AND GAONI, Y., *J. Am. Chem. Soc.*, 83, 4863 (1961).

<sup>47</sup> BRESLOW, R., AND YUAN, C., *J. Am. Chem. Soc.*, 80, 5991 (1958).

<sup>48</sup> WEST, R., AND POWELL, D. L., *J. Am. Chem. Soc.*, 85, 2577 (1963).

<sup>49</sup> BROWN, H. C., AND NELSON, K. L., *J. Am. Chem. Soc.*, 75, 6292 (1953).

<sup>50</sup> WOODWARD, R. B., ROSENBLUM, M., AND WHITING, M. C., *J. Am. Chem. Soc.*, 74, 3458 (1952).

**READING MATERIALS:** A variety of laboratory manuals; "Organic Syntheses";<sup>51</sup> Beilstein;<sup>52</sup> and the original literature.

### Assignments

1. Prepare triphenylcarbinol<sup>53</sup> from ethyl benzoate and the Grignard reagent (use mimeographed procedure);
2. Prepare the triphenylcarbonium ion (look up procedure);
3. Find or devise a preparation of triphenylmethane;
4. Prepare triphenylmethyl chloride<sup>53</sup> from the carbinol (look up procedure);
5. Prepare *o*- and *p*-nitrophenol<sup>53</sup> from phenol (look up procedure);
6. Prepare *p*-aminophenol<sup>53</sup> from *p*-nitrophenol (use NaBH<sub>4</sub> reduction, Brown and Brown<sup>54</sup> or Fe + HCl, Beilstein);
7. Prepare *p*-methylacetophenone<sup>53</sup> from toluene and acetic anhydride (use mimeographed procedure);
8. Prepare azo dye, e.g., methyl orange (look up procedure);
9. Determine the infrared spectrum of at least one of the above products, and compare with the spectrum of a pure sample;
10. Determine the neutralization equivalent of an unknown acid (look up procedure);
11. Perform one of the following quantitative organic determinations (look up procedure): (a) unsaturation, (b) hydroxyl content, (c) equivalent weight of an ester, (d) molecular weight by the Rast method, (e) ionization constant of an indicator, (f) enol content of ethyl acetoacetate, (g) a glycol using periodate;
12. Write a brief paper (about four pages) on the chemistry involved in any one of the experiments.

### CHEMISTRY 52: REACTION KINETICS AND MECHANISMS (Winter Term—Third Year)

Prerequisites: "Chemical Energy"; "Resonance and Aromaticity"; and 2 terms of calculus.

Sessions: 25, 1-hour meetings, approximately; 20, 3-hour laboratory periods.

Texts: Frost and Pearson;<sup>55</sup> Shriner, Fuson, and Curtin (Shriner)<sup>56</sup>

In addition to the texts, original journal articles and the following books are used as sources for reading assignments: Basolo and Pearson;<sup>57</sup> Eliel;<sup>58</sup> Gould;<sup>59</sup> Hammett;<sup>60</sup> Hine;<sup>61</sup> Ingold;<sup>61</sup> King;<sup>62</sup> Leffler and Gruenwald;<sup>63</sup> Newman;<sup>64</sup> Weissberger;<sup>65</sup> and Wheland.<sup>66</sup>

The concept of a chemical change in process is the focus of this course. Along with the idea of reaction rate, the idea of detailed stereochemical structure is developed, and the two are then used in the elucidation of the pathways of certain important reactions. The first few lectures of the course and about 50% of the laboratory time are devoted to qualitative organic analysis. Four single unknowns are assigned, with one usually not listed in the Shriner, Fuson, and Curtin text. Students are thus encouraged to use the reference volumes by Rodd,<sup>67</sup> Huntress,<sup>68, 69</sup> Mulliken,<sup>70</sup> Heilbron,<sup>71</sup> and Beilstein.<sup>52</sup> A few true unknowns are also used, either from unlabeled bottles or from unresolved problems in other laboratory work. Special sessions are scheduled for discussion of the problems at the end of chapters in

<sup>51</sup> "Organic Synthesis," John Wiley & Sons, Inc., New York.

<sup>52</sup> BEILSTEIN, F. K., "Handbuch der organischen Chemie," Springer-Verlag, Berlin.

<sup>53</sup> A sample is required for this substance.

<sup>54</sup> BROWN, C. A., AND BROWN, H. C., *J. Am. Chem. Soc.*, 84, 2829 (1962).

<sup>55</sup> FROST, A. A., AND PEARSON, R. G., "Kinetics and Mechanism," 2nd ed., John Wiley & Sons, Inc., New York, 1961.

<sup>56</sup> SHRINGER, R. L., FUSON, R. C., AND CURTIN, D. Y., "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, Inc., New York, 1956.

<sup>57</sup> BASOLO, F., AND PEARSON, R. G., "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, 1958.

<sup>58</sup> ELIEL, E. L., "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, 1962.

<sup>59</sup> GOULD, E. S., "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, 1959.

<sup>60</sup> HAMMETT, L. P., "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940.

<sup>61</sup> INGOLD, C. K., "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, 1953.

<sup>62</sup> KING, E. L., "How Chemical Reactions Occur," W. A. Benjamin, Inc., New York, 1963.

<sup>63</sup> LEFFLER, J. E., AND GRUENWALD, E., "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, 1963.

<sup>64</sup> NEWMAN, M. S., "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, 1956.

<sup>65</sup> WEISSBERGER, A., Ed., "Technique of Organic Chemistry," Vol. I, Pt. 1, 2nd ed., Interscience Publishers, Inc., New York, 1949.

<sup>66</sup> WHELAND, G. W., "Advanced Organic Chemistry," 3rd ed., John Wiley & Sons, Inc., New York, 1960.

<sup>67</sup> RODD, E. H., Ed., "Chemistry of Carbon Compounds," American Elsevier Publishing Co., Inc., New York, 1962.

<sup>68</sup> HUNTRESS, E. H., AND MULLIKEN, S. P., "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York.

<sup>69</sup> HUNTRESS, E. H., "Organic Chlorine Compounds," John Wiley & Sons, Inc., New York, 1948.

<sup>70</sup> MULLIKEN, S. P., "A Method for Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York.

<sup>71</sup> HEILBRON, L. Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, 1953.

the laboratory text.<sup>56</sup> Periodically throughout the course problems are assigned from the last chapter of this text.

The development of the experimental rate laws and the theories of reactions follows fairly closely the treatment in the kinetics text by Frost and Pearson. Problem assignments are made from this text as well as from separate mimeographed sheets. The focus of the discussion is on a practical understanding of kinetics sufficient to permit the student to read current research articles.

This understanding is put to use in the introductory kinetics experiment in the laboratory. The student studies the effect of concentrations and temperature on the diazo coupling reaction, setting up for himself the procedural details. For approximately the last third of the term, the laboratory time is devoted to a special project in kinetics, with the students working in pairs.

The topics of stereochemistry and nucleophilic substitution are handled in some detail in lectures, since the students have already been exposed to many facets of these topics, and at this stage are ready for a more rigorous presentation. The discussion of nucleophilic substitution leans heavily on the classic article by Streitwieser;<sup>72</sup> but is not as thorough as the fine detail of the review.

The final topics, the Hammett relationship and catalysis, are handled somewhat briefly, but in such a way as to permit the student to understand and apply the basic ideas. By the end of the course the student should be able to read at least the simpler papers dealing with these topics in the current literature.

After the rate laws and rate theories have been studied, the students are assigned a short term paper which is to be based on a recent research article. The students are supplied with a list of possible articles, but are encouraged to look on their own for suitable material. The authors of some of the better term papers are asked to present their topics orally to the class.

#### *Lecture Outline*

- I. **QUALITATIVE ORGANIC ANALYSIS**—4 hours plus several problem-solving sessions (Shriner Chap. 1-7 and 12; Shriner Chap. 8-11, used for reference; Weissberger pp. 70-86; Campbell, *et al.*;<sup>73</sup> Ingold pp. 743-750).
  - A. Physical properties
  - B. Elemental analysis
  - C. Solubility tests
  - D. Acidity and basicity
- II. **THE DESCRIPTION AND MEASUREMENT OF REACTION RATES**—4 hours (Frost and Pearson Chap. 1-3; King Chap. 1-4; Hecht;<sup>74</sup> Tobey.<sup>75</sup>)
  - A. Definitions
  - B. Factors affecting rate
  - C. First and second order rate laws
  - D. Experimental source of rate data
- III. **THEORIES OF REACTION RATES**—4 hours (Frost and Pearson Chap. 4-6; King Chap. 5; Newman pp. 538-555; Leffler and Gruenwald Chap. 4).
  - A. Collision theory
  - B. Activation energy
  - C. Transition state theory
    - 1. Derivation
    - 2. Relationship to collision theory
    - 3. Use of  $E_a$  in explaining phenomena
- IV. **STEREOCHEMISTRY**—5 hours (Wheland Chap. 6 and 7; Mislow and Hopps;<sup>76</sup> Gillespie and Nyholm;<sup>77</sup> Orloff;<sup>78</sup> Eliel pp. 204-219; Collins and Christie).<sup>79</sup>

<sup>72</sup> STREITWIESER, A., *Chem. Rev.*, 56, 573-641 (1956).

<sup>73</sup> CAMPBELL, K. N., ST. CHARLES, M., AND CAMPBELL, B. K., *J. Chem. Educ.*, 27, 261 (1950).

<sup>74</sup> HECHT, C. E., *J. Chem. Educ.*, 39, 311 (1962).

<sup>75</sup> TOBY, S. W., *J. Chem. Educ.*, 39, 473 (1962).

<sup>76</sup> MISLOW, K., AND HOPPS, H. B., *J. Am. Chem. Soc.*, 84, 3018 (1962).

<sup>77</sup> GILLESPIE, R. J., AND NYHOLM, R. S., *Quart. Rev. (London)*, 11, 339 (1957).

<sup>78</sup> ORLOFF, H. D., *Chem. Rev.*, 54, 347 (1954).

<sup>79</sup> COLLINS, C. J., AND CHRISTIE, J. B., *J. Am. Chem. Soc.*, 82, 1255 (1960).

- A. Isomer types
- B. Optical activity
- C. Sugars
- D. Absolute configuration
- E. Stereospecific syntheses
- F. Inorganic stereochemistry
- G. Conformational analysis

V. NUCLEOPHILIC SUBSTITUTION REACTIONS—4 hours (Gould pp. 250-285; Streitwieser;<sup>72</sup> Hine Chap. 6).

- A. *SN1* *versus* *SN2*
- B. Effect of changes in nucleophile, solvent or substrate
- C. Other mechanisms involving a nucleophilic substitution step
- D. Neighboring group participation

VI. HAMMETT EQUATION—2 hours (Gould pp. 220-224; Hammett pp. 184-198).

- A. Linear free energy relationships
- B. Use of *sigma* and *rho* constants

VII. CATALYSIS—2 hours (Hine Chap. 8; Frost and Pearson Chap. 9; Basolo Chap. 7).

- A. General and specific acid or base catalysis
- B. Anion catalysis or redox reactions

*Laboratory Outline* (See introductory paragraph above.)

1. Identification of four unknowns by qualitative analysis—30 hours (Shriner).
2. Effect of concentration and temperature on the rate of a diazo coupling reaction—10 hours.
3. Kinetics project—devised by the student with help available from the instructor—20 hours.

### CHEMISTRY 53: BIOCHEMISTRY (Spring Term—Third or Fourth Year)

Prerequisite: "Resonance and Aromaticity."

Sessions: 30, 1-hour classes; approximately 30 hours of laboratory.

Text: Fruton and Simmonds (Fruton).<sup>80</sup> Reading materials: Neurath and Bailey;<sup>81</sup> Boyer, Lardy and Myrback;<sup>82</sup> Colowick and Kaplan;<sup>83</sup> Cook;<sup>84</sup> Noller.<sup>85</sup>

Since this course is not as integral a part of the curriculum as are the other courses, its content can vary considerably with different instructors. The following outline was used in 1963. In 1964 the course will contain a good deal more physical chemistry. Several factors do remain constant, however. One is the emphasis on the original literature; another is the emphasis on the chemical aspects of biochemistry rather than on the medical or biological aspects.

At the end of the term the student is expected to present a term paper on an enzyme he has chosen. This paper is expected to be a definitive review of what is known of the particular enzyme. In the case of a thoroughly studied enzyme, some aspect of its chemistry is to be reviewed. Such an assignment cannot be carried out with all enzymes; therefore the student is given some help in his choice. Primary sources are required when available in the library.

*Lecture Outline* (used in 1963)

- I. INTRODUCTION—1 hour.
  - A. Definitions (Fruton Chap. 1)
  - B. Enzymes (Asimov)<sup>86</sup>
- II. PROTEINS.
  - A. Classification—1 hour (Fruton Chap. 2; Vickery)<sup>87</sup>

<sup>80</sup> FRUTON, J. S., AND SIMMONDS, S., "General Biochemistry," 2nd ed., John Wiley & Sons, Inc., New York, 1959.

<sup>81</sup> NEURATH, H., AND BAILEY, K., Ed's, "The Proteins," Academic Press, Inc., New York, 1953.

<sup>82</sup> BOYER, P. D., LARDY, H., AND MYRBACK, K., Ed's, "The Enzymes," 2nd ed., Academic Press, Inc., New York, 1959.

<sup>83</sup> COLOWICK, S. P., AND KAPLAN, N. O., Ed's, "Methods in Enzymology," Academic Press, Inc., New York, 1957.

<sup>84</sup> COOK, J. W., Ed., "Progress in Organic Chemistry," Butterworth & Co., Ltd., London, 1958.

<sup>85</sup> NOLLER, C. R., "Chemistry of Organic Compounds," 2nd ed., W. B. Saunders Co., Philadelphia, 1957.

<sup>86</sup> ASIMOV, I., *J. Chem. Educ.*, 36, 535 (1959).

<sup>87</sup> VICKERY, H. B., *J. Chem. Educ.*, 19, 73 (1942).

- B. Particle size and shape—2 hours (Fruton pp. 148-161; "The Proteins," IB, Chap. 7; Craig, *et al.*)<sup>88</sup>
- C. Isolation and purification—3 hours (Fruton Chap. 3 and 4; Julian, *et al.*,<sup>89</sup> Colvin, *et al.*,<sup>90</sup> "The Proteins," IA, Chap. 1; IB, Chap. 9; Anthony,<sup>91</sup> Tanford and Hauenstein)<sup>92</sup>
- D. Protein hydrolysis—3 hours (Fruton Chap. 5, 8, 29, 30, and pp. 272-279; Smith and Spackman,<sup>93</sup> Colowick and Kaplan, Vol. III, pp. 504-528)
- E. Determination of amino acid sequence—1 hour (Cook and Harris,<sup>94</sup> Moore and Stein *et al.*)<sup>95, 96</sup>
- F. Protein and peptide synthesis—5 hours (Fruton Chap. 7 and 9; Fairley,<sup>97</sup> Allen, *et al.*,<sup>98, 99</sup> Kruh, *et al.*,<sup>100</sup> Doctor, *et al.*,<sup>101</sup> Simpson,<sup>102</sup> Watson)<sup>103</sup>

### III. CARBOHYDRATES.

- A. Structure—2 hours (Fruton Chap. 16 and 17; Noller Chap. 17; Ferrier and Overend)<sup>104</sup>
- B. Complex carbohydrates—4 hours (Fruton Chap. 18; Larner, *et al.*)<sup>105, 106, 107</sup>
- C. Metabolism—2 hours (Fruton Chap. 19; Gunsalus, *et al.*)<sup>108</sup>
- D. Krebs cycle—3 hours (Fruton Chap. 20; Stern and Ochoa,<sup>109</sup> Siebert, *et al.*,<sup>110</sup> Sanadi *et al.*,<sup>111</sup> Rose)<sup>112</sup>
- E. Electron transport system—2 hours (Hendlin and Cook,<sup>113</sup> Green and Hatefi)<sup>114</sup>
- F. Lipids—1 hour (Fruton Chap. 23-25)

#### Laboratory Outline

The laboratory work which can be done in thirty hours is limited; therefore an assignment was tried in 1963 which did not give a comprehensive view of biochemical laboratory work, but which did satisfy another important goal. The student had to think about procedure and experimental design and make his own decisions about them. The student acquired valuable experience with colorimetry, chromatography, and other basic operations of biochemical research, plus an introduction to a real research problem. The assignment was to prepare a protein, pure, crystalline if possible, and in reasonable yield; demonstrate its purity by at least one method; and then hydrolyze the protein and demonstrate the presence of at least 10 different amino acids. Suggestions were made as to proteins suitable for this assignment.

#### CHEMISTRY 54: THERMODYNAMICS (Fall Term—Fourth Year)

Prerequisites: Chemistry 50 and 52; and 2 terms of calculus.

Sessions: 30, 1-hour classes; 20, 3-hour laboratory periods.

TEXT: Barrow.<sup>21</sup>

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- <sup>88</sup> CRAIG, L. C., KING, T. P., AND STRACHER, A., *J. Am. Chem. Soc.*, 79, 3729 (1957).
- <sup>89</sup> JULIAN, G. R., WOLFE, R. G., AND REITHEL, F. J., *J. Biol. Chem.*, 236, 754 (1961).
- <sup>90</sup> COLVIN, J. R., SMITH, D. B., AND COOK, W. H., *Chem. Rev.*, 54, 687 (1954).
- <sup>91</sup> ANTHONY, D. S., *J. Chem. Educ.*, 36, 540 (1959).
- <sup>92</sup> TANFORD, C., AND HAUENSTEIN, J. D., *J. Am. Chem. Soc.*, 78, 5287 (1956).
- <sup>93</sup> SMITH, E. L., AND SPACKMAN, D. H., *J. Biol. Chem.*, 212, 271 (1955).
- <sup>94</sup> COOK, A. H., AND HARRIS, G., "Progress in Organic Chemistry," Cook, J. W., Ed., Vol. IV, p. 140, Butterworth & Co., Ltd., London, 1958.
- <sup>95</sup> HIRS, C. H. W., MOORE, S., AND STEIN, W. H., *J. Biol. Chem.*, 235, 633 (1960).
- <sup>96</sup> SPACKMAN, D. H., STEIN, W. H., AND MOORE, S., *J. Biol. Chem.*, 235, 648 (1960).
- <sup>97</sup> FAIRLEY, J. L., *J. Chem. Educ.*, 36, 544 (1959).
- <sup>98</sup> ALLEN, E. H., GLASSMAN, E., AND SCHWEET, R. S., *J. Biol. Chem.*, 235, 1061 (1960).
- <sup>99</sup> ALLEN, E. H., GLASSMAN, E., CORDES, E., AND SCHWEET, R. S., *J. Biol. Chem.*, 235, 1068 (1960).
- <sup>100</sup> KRUH, J., DREYFUS, J. C., AND SCHAPIRA, G., *J. Biol. Chem.*, 235, 1075 (1960).
- <sup>101</sup> DOCTOR, B. P., AFGAR, J., AND HOLLY, R. W., *J. Biol. Chem.*, 236, 1117 (1961).
- <sup>102</sup> SIMPSON, M. V., *Ann. Rev. Biochem.*, 31, 333 (1962).
- <sup>103</sup> WATSON, J. D., *Science*, 140, 17 (1963).
- <sup>104</sup> FERRIER, R. J., AND OVEREND, W. G., *Quart. Rev.*, 13, 265 (1959).
- <sup>105</sup> CORI, G. T., AND LARNER, J., *J. Biol. Chem.*, 188, 17 (1951).
- <sup>106</sup> LARNER, J., ILLINGWORTH, B., CORI, G. T., AND CORI, C. F., *J. Biol. Chem.*, 199, 641 (1952).
- <sup>107</sup> LARNER, J., *J. Biol. Chem.*, 202, 491 (1953).
- <sup>108</sup> GUNSALUS, I. C., BARTON, L. S., AND GRUBER, W. J., *J. Am. Chem. Soc.*, 78, 1763 (1956).
- <sup>109</sup> STERN, J. R., AND OCHOA, S., *J. Biol. Chem.*, 198, 313 (1952).
- <sup>110</sup> SIEBERT, G., CARSOTIS, M., AND PLAUT, G. W. E., *J. Biol. Chem.*, 226, 977 (1957).
- <sup>111</sup> SANADI, D. R., LANGLEY, M., AND WHITE, F., *J. Biol. Chem.*, 234, 183 (1959).
- <sup>112</sup> ROSE, Z. B., *J. Biol. Chem.*, 235, 928 (1960).
- <sup>113</sup> HENDLIN, D., AND COOK, T. M., *J. Biol. Chem.*, 235, 1187 (1960).
- <sup>114</sup> GREEN, D. E., AND HATEFI, Y., *Science*, 133, 13 (1961).

### Lecture Outline

Discussions of energy are worked out in more rigorous fashion than in Chemistry 50, and a number of additional relationships are explored through the use of partial derivatives. A major object of the study is to link statistical mechanics to thermodynamics. The two points of view are therefore developed together. The degrees of freedom of gas molecules are discussed, and the role of quantized vibrational energy levels is developed. Special attention is given to the analysis of chemical reactions by means of ideas about energy.

- I. KINETIC-MOLECULAR THEORY—7 hours (Chap. 1, 2, and 3—Sect. 3-12 to 3-18).<sup>115</sup>
- II. ENERGY—3 hours (Chap. 4 and 5; see also Everett).<sup>116</sup>
- III. ENTROPY—6 hours (Chap. 6 and 7; see also: Luder;<sup>117, 118</sup> Fast;<sup>119</sup> Lewis and Randall Chap. 7 and 8).<sup>120</sup>
- IV. HETEROGENEOUS EQUILIBRIA—6 hours (Chap. 12 and 14).
- V. SOLUTIONS—9 hours (Chap. 15, 16, 17, and 18).

### Laboratory Work

No assigned text is used but references are made to a variety of published laboratory books. Some relatively conventional physical chemistry experiments are used. In most cases, the students assemble all or a large part of their apparatus. Experiment write-ups devote major attention to an analysis of errors. A new type of experiment is being tried wherein the student is assigned a reaction system, and asked to obtain thermodynamic data sufficient to provide a basis for choosing among alternative interpretations of the reaction. For example, in the reaction of  $\text{Cu}^{2+}$  (aq) with  $\text{NH}_3$ , is it reasonable to conclude that electrostatic repulsion or entropy controls the reaction?

Experiments include vapor density and molecular mass; gaseous effusion and molecular mass; velocity of sound and molecular complexity; and interpretation of a chemical reaction system by means of enthalpy, entropy, and free energy data.

### CHEMISTRY 55: PERIODICITY AND STRUCTURE (Fall Term—Fourth Year)

Prerequisites: "Ions"; "Chemical Energy"; "Resonance and Aromaticity"; and "Kinetics."

Sessions: 30, 1-hour meetings; 19, 3-hour laboratory periods.

References Sources: Harvey and Porter;<sup>121</sup> Basolo and Pearson;<sup>57</sup> Gould;<sup>122</sup> Gilreath;<sup>123</sup> Sanderson;<sup>124</sup> Latimer;<sup>22</sup> Cartmell and Fowles.<sup>125</sup>

This course is designed to supplement and broaden the students' knowledge of structure and reactions throughout the periodic table. An effort is made to systematize the stereochemistry within the framework of periodic relationships, and to utilize the students' previous knowledge in the areas of atomic and molecular structure, reaction mechanisms, and experimental methods of investigation. It is anticipated that content will vary from year to year; however, as presently taught, the major focus is on the chemistry of the transition elements. Study of these elements brings in a considerable variety of geometrical configurations, some important examples of reaction mechanisms, a number of physical methods, and perhaps most important, focuses on an area in which rapid advances are currently being made in the correlation of stereochemistry and electronic configuration.

<sup>115</sup> All references are to Barrow, "Physical Chemistry,"<sup>21</sup> unless otherwise noted.

<sup>116</sup> EVERETT, D. H., "Chemical Thermodynamics," Longmans, Green and Co., Ltd., London, 1959.

<sup>117</sup> LUDER, W. F., *J. Chem. Educ.*, 23, 54 (1946).

<sup>118</sup> LUDER, W. F., *J. Chem. Educ.*, 23, 110 (1946).

<sup>119</sup> FAST, J. D., "Entropy," McGraw-Hill Book Co., Inc., New York, 1962, pp. 88-106.

<sup>120</sup> LEWIS, G. N., AND RANDALL, M., (Revised by PRIZER, K. S., AND BREWER, L.) "Thermodynamics," 2nd ed., McGraw-Hill Book Co., Inc., New York 1961.

<sup>121</sup> HARVEY, K. B., AND PORTER, G. B., "Introduction to Physical Inorganic Chemistry," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1963.

<sup>122</sup> GOULD, E. S., "Inorganic Reactions and Structure," 2nd ed., Holt, Rinehart, and Winston, Inc., New York, 1962.

<sup>123</sup> GILREATH, E. S., "Fundamental Concepts of Inorganic Chemistry," McGraw-Hill Book Co., Inc., New York, 1958.

<sup>124</sup> SANDERSON, R. T., "Chemical Periodicity," Reinhold Publishing Corp., New York, 1960.

<sup>125</sup> CARTMELL, E., AND FOWLES, G. W. A., "Valency and Molecular Structure," 2nd ed., Butterworth & Co., Ltd., London, 1961.

In addition to the major emphases of periodicity and structure, two other topics are included in the course, largely for reasons of convenience. The first is some additional discussion on methods of chemical analysis, supplementing the discussion of this topic in the "Ions" course. The second is an introduction to radiochemistry, with emphasis on the utilization of radiochemical techniques in the study of chemical systems.

Two library papers are required. The first is an investigation of possible methods of analysis for an assigned compound, using the original literature as well as secondary sources, and emphasizing evaluation of the different methods. The second is on some recent development in chemical structure, such as boron hydrides, inorganic polymers, noble gas compounds, metal olefin compounds, ligand field theory, inorganic free radicals, etc.

#### *Lecture Outline*

- I. ATOMIC STRUCTURE AND PERIODICITY (Harvey and Porter Chap. 3; Gilreath Chap. 2 and 3).
  - A. Historical review of developments leading up to the quantum theory
  - B. Wave mechanics; partial solution of the hydrogen atom wave equation
  - C. Electronic configuration and periodic properties
- II. INTRODUCTION TO COORDINATION CHEMISTRY (Harvey and Porter Chap. 6; Gilreath Chap. 5).
  - A. Historical development
  - B. General survey of common ligands
  - C. Stereochemistry
    - 1. Geometrical configurations
    - 2. Geometrical and optical isomerism
  - D. Magnetic susceptibility
  - E. Complex ions in biochemistry, analysis, catalysis, etc.
- III. BONDING IN COORDINATION COMPOUNDS (Basolo and Pearson Chap. 2).
  - A. Valence bond theory
  - B. Ligand field theory
  - C. Molecular orbital theory
  - D. Comparison of theories
    - 1. Correlation with magnetic properties
    - 2. Stabilization effects
  - E. Ligand field strength and types of ligands
  - F. Jahn-Teller theorem
  - G. Tetragonality of  $d^8$  ions
- IV. CHEMISTRY OF THE TRANSITION ELEMENTS (Gould Chap. 11, 21, and 24).
  - A. Group I-B
  - B. Groups VI-B and VII-B
  - C. Group VIII-B
- V. REACTION MECHANISMS (Harvey and Porter Chap. 10).
  - A. Review of kinetic methods
  - B. Oxidation-reduction reactions
    - 1. Atom transfer
    - 2. Electron transfer
- C. SUBSTITUTION REACTIONS OF COORDINATION COMPOUNDS.
  - 1.  $S_N1$  and  $S_N2$  mechanisms
  - 2. Hydrolysis and anation reactions
  - 3. Racemization reactions
- VI. SURVEY OF STEREOCHEMISTRY BY PERIODIC GROUPS (Gillespie and Nyholm).<sup>126</sup>
- VII. RADIOCHEMISTRY (Gould Chap. 27).
  - A. Types of radiation and methods of detection
  - B. Nuclear energy
  - C. Applications of radioisotope methods to the study of chemical systems

<sup>126</sup> GILLESPIE, R. J., AND NYHOLM, R. S., "Quart. Revs.", 11, 339 (1957).

### Laboratory Program

1. Preparation of four typical metal coordination compounds and determination of their magnetic susceptibilities (mimeographed) (2½ sessions): (a) hexammine-nickel(II) chloride, (b) potassium tetracyanonickelate(II), (c) *tris*-ethylenediamine-cobalt(III) chloride, (d) *tris*-acetylacetone-iron(III); 2. Preparation of chromium(II) acetate—unstable oxidation state—preparation carried out under an inert atmosphere (Walton p. 161) (1 session); 3. Preparation of liquid dinitrogen tetroxide—glass work, handling of a volatile liquid (mimeographed) (½ session); 4. Introduction to radioisotope techniques (mimeographed) (3 sessions): (a) counting techniques, (b) demonstration of dynamic equilibrium, (c) a study of coprecipitation, (d) neutron activation and determination of half-life; 5. Resolution of *tris*-ethylenediamine-cobalt(III) ion into optical isomers, followed by polarimetric studies of the rate of racemization (mimeographed) (2 sessions); 6. Spectrophotometric continuous variations study of the copper(II)-ethylenediamine system (mimeographed) (1 session); 7. Spectrophotometric studies of crystal field stabilization energies (mimeographed) (2 sessions)—either (a) nickel(II) with various ligands, or (b) series of metal ions with a single ligand; 8. Preparation of several individually assigned compounds followed by appropriate characterization studies such as magnetic susceptibilities, solution conductivities, and spectra (recording ultraviolet, visible, and infrared spectrometers are available) (4 sessions); 9. A study of a reaction mechanism, including composition and rate data (students work in groups) (3 sessions).

### CHEMISTRY 80: CHEMISTRY SEMINAR (Winter Term—Fourth Year)

Three aims are served by the senior seminar in chemistry. (1) Each student carries out a literature search and often does preliminary experiments in preparation for his third-term independent study project. Alternatively, if he has done some independent study earlier, he is expected to do further work, and perhaps present a report of his work to the seminar. (2) Students and staff discuss recent published research, chosen to help integrate and broaden the student's four-year chemistry experience. (3) Students are expected to prepare themselves for the comprehensive examination to be taken during the following term.

During 1963, seminar discussions for the first half of the term were based on M. J. S. Dewar's book, "Hyperconjugation."<sup>127</sup> Students reported on primary literature, basic to, or referred to in the book. In 1964 H. Hyman's "The Noble Gas Compounds"<sup>128</sup> was used as the focus for part of the literature reports. Both books demonstrate the use of a variety of techniques in the study of a small set of phenomena.

### CHEMISTRY 85: INDEPENDENT STUDY (Spring Term—Fourth Year)

The chemistry major carries on a program of independent study, usually involving experimental research, and most often related to the research interests or programs of a staff member. Preliminary work is normally begun in Chemistry 80. At the end of the term the student submits a paper incorporating his experimental findings and interpretations, written according to the style of published journal articles. Many chemistry majors complete the requirements for this course by carrying out research in a summer research participation program.

<sup>127</sup> DEWAR, M. J. S., "Hyperconjugation," Ronald Press Co., New York, 1962.

<sup>128</sup> HYMAN, H. H., "The Noble Gas Compounds," University of Chicago Press, Chicago, 1963.

## VI. THE HARVARD EXPERIMENT

L. K. Nash described informally a novel experiment being carried on at Harvard University. The description which follows is based on notes taken by several of the conference participants supplemented by materials kindly provided by E. B. Wilson and E. J. Corey of Harvard.

In this experiment, a group of twenty-five selected students has been put through, in two years, a series of four special courses which it is expected will give them adequate preparation to enter senior and graduate electives by the beginning of the junior year. The more usual sequence of six to eight semesters, comprising general chemistry, elementary quantitative analysis, organic and physical chemistry, is replaced by four semesters taught respectively by W. N. Lipscomb, E. J. Corey, F. H. Westheimer, and E. B. Wilson. The teaching approach is based on the assumptions that (1) carefully selected students are capable of a great deal more than is usually assumed, (2) nothing needs to be taught twice, and (3) there is little point in teaching what can be read. As a result, a wide variety of reading matter is given to the students including books ordinarily used at the senior and graduate level. Programmed instruction has been developed, and is utilized where it is felt this is the most efficient and economical means of instruction. Lectures emphasize only the most important points. Each semester the group of twenty-five students is taught directly by a full professor, assisted by an instructor and two teaching fellows. Besides the class and conference periods, there are each week two three-hour laboratory periods.

The first semester taught by W. N. Lipscomb emphasizes physical, theoretical, inorganic, and some quantitative aspects of chemistry. The principal topics are (a) wave properties of matter, (b) transition metals and rare earths, and (c) thermodynamics. The authors suggested as suitable for background reading are Linnett,<sup>1</sup> Coulson,<sup>2</sup> Orgel,<sup>3</sup> Cotton and Wilkinson,<sup>4</sup> and Moore.<sup>5</sup>

The laboratory experiments in this first semester of chemistry emphasize how sharp the break is that has been made with tradition. The first experiment at the start of the term is a study of standing sound waves in a three-dimensional enclosure, in which the students determine an experimental frequency spectrum, and apply the wave equation in one and three dimensions. The wave concept is then applied to electrons in metals, and the Schrödinger equation is developed as a practical thing rather than as an abstraction. Another experiment involves exploration of the relationships involved in molecular structure, bond angles and distances, isomerism, and modes of packing, using cork balls and connecting rods to build models. A spectroscopic experiment is done in which the simple Spectranal<sup>6</sup> exhibits a spectroscopic line series which is analyzable and allows qualitative analysis of metal samples. Chemical equilibrium and complex formation is approached by a spectrophotometric study of the ferric sulfosalicylate system, using the method of continuous variations. Programmed instruction is given on Beer's law, Job's method of continuous variations, and the law of mass action. The spectrochemical series is studied by measurement of the absorption spectra of three cobaltic complexes, and interpretation of the wavelengths of maximum absorption in terms of ligand field theory. Further experience in mass action and in simple quantitative techniques is obtained through a spectrophotometric study of mixtures of cupric salts with ammonia in aqueous solution. With the aid of programmed instruction on analysis of complex mixtures and the theory of consecutive complex formation, the students interpret the absorption curves, calculate extinction coefficients, and plot the distribution of the several complexes in the mixture. Chemical separations are illustrated by an ion exchange separation of copper and zinc with quantitative determination of the constituents by EDTA titration.

The second semester, devoted to physical and organic chemistry and taught by F. H. Westheimer, emphasizes kinetics and mechanisms. Recommended books are Fieser and Fieser,<sup>7</sup> and Cram and Hammond.<sup>8</sup>

<sup>1</sup> LINNETT, J. W., "Wave Mechanics and Valency," John Wiley & Sons, Inc., New York, 1960.

<sup>2</sup> COULSON, C. A., "Valence," 2nd ed., Oxford University Press, New York, 1961.

<sup>3</sup> ORGEL, L., "An Introduction to Transition-Metal Chemistry," John Wiley & Sons, Inc., New York, 1960.

<sup>4</sup> COTTON, F. A., AND WILKINSON, G., "Advanced Inorganic Chemistry," Interscience (John Wiley & Sons, Inc., New York), 1962.

<sup>5</sup> MOORE, W. J., "Physical Chemistry," 3rd ed., Prentice-Hall, Inc., 1962.

<sup>6</sup> Available from Fisher Scientific Co.

<sup>7</sup> FIESER, L. F., AND FIESER, M., "Organic Chemistry," 3rd ed., Reinhold Publishing Corp., New York, 1956.

<sup>8</sup> CRAM, D., AND HAMMOND, G. S., "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1959.

The laboratory experiments include the preparation of cholesterol from gallstones, and the preparation of *tris*-ethylenediamine-cobalt(III) complexes, with resolution into diastereoisomers with tartaric acid. The determination of the purity of the compounds serves as an illustration of iodometric analysis. A third experiment involves the preparation of desoxybenzoin and its deuterated analogues, followed by deuterium analysis and some determination of rates of reaction with bromine. In the course of the semester the students utilized Friedel-Crafts and Grignard reactions, and employ a spectrophotometer for determining rates of bromination reaction. A base-catalyzed exchange with heavy water is also performed.

The third semester, taught by E. J. Corey, emphasizes the physical principles of organic chemistry and their application to synthesis. Among the topics treated are: (1) prediction of equilibria and rates of organic reactions from thermodynamic data and activated complex-absolute rate theory; (2) kinetic criteria of mechanisms; (3) dependence of bond strength on bond angles and hybridization; and (4) effects of steric repulsion and eclipsing. Considerable time is devoted to stereochemistry and conformational analysis. The mechanisms of organic reactions are classified, and detailed surveys are made of nucleophilic displacement, elimination, electrophilic addition and substitution, etc., and their application to synthesis. The laboratory experience includes: (1) the synthesis of a series of related compounds according to Fieser,<sup>9</sup> these being 1,2-diphenylethane derivatives; (2) the preparation of *cis*- and *trans*-4-phenyl-cyclohexanal, and the study of the kinetics of oxidation of these compounds, leading to the determination of the ratio of axial and equatorial configurations; and (3) analysis and identification of mixtures of unknowns. The students separate and purify, classify and identify the compounds. They are given quantitative elementary analysis data and also provided with nuclear magnetic resonance and infrared spectra.

The fourth semester, taught by E. B. Wilson, concentrates on physical chemistry, largely from the standpoint of statistical mechanics. Lectures begin with a rapid summary of quantum mechanical principles, which were introduced previously. The energy levels and degeneracies for the particle in a box, the rigid rotor, and the harmonic oscillator are briefly discussed. Quantum statistical mechanics is introduced in the normal manner, and the most probable distribution function for an ideal gas is derived. The thermodynamic properties are expressed in terms of the partition function. The Maxwell-Boltzmann distribution law for molecular velocities is introduced next, and it is made the basis of a brief treatment of the kinetic theory of gases. Going back to statistical mechanics, the partition functions for simple molecular models are derived. The first and second laws of thermodynamics are discussed from a statistical mechanical viewpoint. The statistical mechanical treatment of general systems other than gases is derived. Entropy, free energy, conditions for equilibrium, and chemical equilibrium constants for gaseous reactions are the next topics, all from a statistical mechanical approach.

First law ideas and discussions of heats of reaction, etc., were included in earlier portions of this course. At this point the subject is reviewed, and an effort is made to show the relationship between classical thermodynamic and statistical mechanical viewpoints. The third law of thermodynamics and the treatment of crystals is also taken up.

The laboratory work involves twelve experiments, five of which are from Shoemaker and Garland:<sup>10</sup> gas thermometry, heat of vaporization, chloroform-acetone phase diagram, low temperature heat capacity, and gas kinetics (decomposition of 2,5-dihydrofuran). The remaining experiments are critical density of CO<sub>2</sub>, heats of dilution of HCl, the silver-silver chloride—HCl cell, Johnson noise in a resistor, magnetic susceptibility of paramagnetic substances, viscosity of gases, and zone refining of a two-component system. These are described in special write-ups. The students are taught to use a Fortran program with the IBM 1620 computer for the least squares determination of the liquid and vapor densities of carbon dioxide in the critical density experiment.

Two groups of students have passed through the entire cycle and their progress in advanced courses is being watched with interest. The Harvard people are convinced now of the feasibility of this opera-

<sup>9</sup> FIESER, L. F., "Experiments in Organic Chemistry," 3rd ed., D. C. Heath & Co., Boston, 1957.

<sup>10</sup> SHOEMAKER, D. P., AND GARLAND, C. W., "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1962.

tion, but they recognize that relatively few students are able and willing to proceed at this pace. The whole program is being evaluated in terms not only of the degree of success achieved with the students, but of the very large expenditure of staff time and departmental facilities involved in the education of a relatively small number of students. At the time of writing, the experiment is being continued, but the long-range status of the program is not yet clear.

## VII. SUMMARY AND CONCLUSIONS

The group first undertook to identify the principal concerns which are motivating the introduction of curriculum changes. The reasons cited varied considerably from department to department and reflected specific local conditions, the size and nature of the institution, and the constraints peculiar to each situation. However, a number of reasons given were common to many if not all departments. The view was generally expressed that the traditional sequence of subjects was historical, rather than logical, and was no longer an efficient program for providing a modern chemical education. The most frequently voiced concern was the problem how best to handle students with superior high school preparation in chemistry, mathematics, and physics. Students now enter college usually with one of three dissimilar high school preparations in chemistry: the CBA, the CHEM Study, or the traditional. A certain number, of course, come with no preparation at all. The heterogeneity of high school preparation creates one type of problem now. If, as seems likely, a substantial percentage of entering students will have had CBA, CHEM Study, or some other improved training in the near future, a different, but equally urgent, problem will be created.

High school preparation is but one aspect of the broader problem of the teaching of general chemistry as such. The questions of what form general chemistry should have, and how many kinds should be offered in a given institution, are some of the major topics for debate. A decided improvement in the mathematical preparation of most entering students makes possible early introduction of physical principles based on mathematical reasoning, and this was felt to be most desirable. The increasing trend of physical chemistry to "trickle down" into the first year is very apparent, but it is not clear how far it is actually desirable to go in this direction, nor what should be removed to provide time (the problem of constant volume).

The general chemistry laboratory is a particularly vexing problem. Everyone agrees that it should be significant and provide motivation, but the effective processes for accomplishing this have not yet been identified clearly. (It should be noted that the Advisory Council on College Chemistry has a committee working actively on this general problem, and it is recognized to be one of the most urgent confronting colleges and universities today.) There was general agreement that current efforts to improve high school chemistry should be given encouragement so that the colleges could have a sound base to build on. It was felt also that the first course in college chemistry should have a form which clearly distinguished it from the high school course, in order that the students would not feel they were being put through the same process twice.

During the discussion it became evident that extensive revision of the first year, such as by introducing substantial amounts of physical principles, bonding theory, organic chemistry, or quantitative analytical techniques in the laboratory, will not only permit, but necessitate, considerable revision of the subsequent courses. Considerable change is already taking place, and the extent to which the content of many of the sophomore, junior, and senior courses has altered in the last fifteen years is truly surprising. Large areas of subject matter have shifted sub-disciplines through changes in interest and emphasis. The teaching of ionic equilibrium and electrochemistry, for example, has moved from physical to analytical courses in many institutions, and kinetics is frequently now considered the province of the organic chemist. There was much discussion of the blurring of boundaries, particularly between organic and physical chemistry. One institution is considering having a single laboratory for organic and physical chemistry! A trend was noted for the interests of physical chemists to move either in the direction of physical-organic or toward chemical-physics, leaving many of the topics of classical physical chemistry to be the concern of analytical and inorganic chemists, who have research interests in those areas. Concurrently, many topics in physics are becoming primarily the province of physical chemists.

A need was recognized for a careful re-examination of the organization of topics throughout the entire curriculum in order that serious gaps, as well as needless duplication, be avoided. While some repetition is pedagogically desirable, it seems hardly necessary to go over ionic equilibria, atomic structure, and chemical bonding, for example, in three or even four separate courses. Significant gains in efficiency could be possible by intelligent reapportioning.

There was a general sentiment that something should be done about the course in classical quantitative inorganic analysis traditionally given in the sophomore year. The need for upgrading it in some

way is strongly felt, and it was also argued that up-to-date fundamental analytical chemistry cannot be taught effectively at the sophomore level, and it should be given at a later point in the curriculum. The conversion of freshman chemistry to a general chemistry based on physical principles leaves a serious gap in the inorganic background of the student. The question of how to improve the level of presentation of inorganic chemistry, or even reintroduce it into the curriculum, was felt to be important. The primary problems concerned with organic chemistry appear to be how much to emphasize the physical basis of organic reactions, and how early to begin the study of organic chemistry in the curriculum.

The fact that a greater percentage of chemistry students is going on to graduate school was recognized, and it was agreed that a responsibility exists to take this into consideration in designing the undergraduate curriculum. The amount of time spent in getting a Ph.D. varies considerably with field and school, but there was a general feeling that it need not be as long as it often is if the undergraduate years could be used to best advantage. A primary concern expressed by everyone was the need to select material and teach it effectively so that the fundamental undergraduate training could be presented in a reasonable amount of time. The objective of making it possible for the chemistry major to complete a core program by the end of his junior year was rather generally agreed upon. This core would include organic, physical, analytical and inorganic, with the latter two preferably following and based upon physical chemistry. The senior year should be free for advanced courses and research. The importance of research experience was agreed upon, and the advantage of the student being able to spend the summer before his senior year in such activity was attested to by many.

The problems concerned with the achievement of a three year core were recognized as being considerable, particularly in institutions which insist that a large fraction of the students' nonprofessional education come in the first two years. In general, it would seem to be possible without reducing the student's traditional exposure to the humanities and social sciences if this exposure can be spread over a reasonable length of time.

The importance of the liberal arts college as a source of students going on to graduate work in chemistry was repeatedly cited. The liberal arts colleges traditionally supply not only a large percentage of the students who go on to graduate school, but many of the best students as well. The liberal arts colleges have also been particularly active in originating new and stimulating approaches to the teaching of chemistry. Considerable concern was expressed about the problems of the liberal arts college department which is often caught between the institution's policy of emphasizing diversity and distribution, and the practical pressures involved in giving a professional education which meets national standards. There are physicists already who say that no one can hope to become a theoretical physicist unless he starts at a great university rather than at a small college. It is possible to visualize developments in the undergraduate chemistry curriculum which could lead to a similar situation, and it was unanimously agreed that this would be unfortunate and undesirable. Curriculum developments should lead to a flexibility which allows students to prepare for graduate school in a variety of institutions, as at present. The group agreed that the Council should recommend to the American Chemical Society Committee on Professional Training that it reconsider its minimum standards in the light of increasing emphasis on preparation for graduate work and the need of encouraging new curricular developments.

A diversity of approaches to the teaching of chemistry was agreed to be a good and a healthy thing. Certain of the approaches, such as the Illinois-MIT plan are particularly well suited to large departments, and especially the departments which operate with more or less clearly defined divisions of inorganic, organic, analytical, and physical chemistry. It was pointed out that the undergraduate courses at such institutions are taught (general chemistry frequently excepted) by individuals with research interests close to the subject matter. Such persons feel a large degree of professional identification with the material they are teaching. The principal problems are coordination, distribution of topics, and arranging the curriculum units in a logical and coherent sequence. The flexibility engendered in a small, closely knit department makes experimentation, such as the Earlham plan, quite feasible, while the introduction of such a curriculum into a large department would appear to present very formidable problems of organization and coordination. Similarly the introduction of a combined physics and chemistry approach seems to be easier in the small department. The Brown plan seems to be quite feasible for either large or small departments.

Any institution which ventures upon radical alteration of the traditional sequence creates a problem for the students who transfer either into, or out of the curriculum. Although on paper the difficulties of the transfer student sometimes seem unsurmountable, experience has shown that the students themselves often have a greater adaptability than we give them credit for, and the changes can be accomplished with surprisingly little difficulty.

The existence of a number of problems which have been inadequately dealt with or left unrecognized was brought out. The increased emphasis on physical principles has tended toward a neglect of important techniques. Not only does the present day student miss getting manipulative practice in the traditional laboratory techniques, which are still of great importance in research (glassblowing and metal working, for example), but experience in the newer methods of electronics and instrumentation seldom comes his way before he has to undertake his research. A lack of manual skills was felt by many to be a significant factor in slowing up graduate research. How much this can be alleviated by undergraduate research experience and what remedy might be found in the crowded undergraduate curriculum is not clear.

The possibilities which might be opened up by a study of the process of teaching chemistry were also considered. There is evidence in the experience of the Earlham participants that an analysis of the structure of the subject to identify basic unifying concepts may allow a systematization which can provide great efficiency and effectiveness in teaching. The potentialities of such an approach appear to be very great.

The conference concluded with a general expression of agreement that all present had benefited by the opportunity to identify clearly the problems involved in modernizing the undergraduate curriculum and to compare several of the most completely developed alternatives. It was urged that information about these experimental curricula and a summary of the discussions and conclusions be made generally available.